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OPIUM ANALYSIS.

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In presenting a method for the analysis of opium, as an addition to the many processes published from time to time, I feel justified on account of the importance which a correct analysis of this costly substance demands. I lay claim to no special originality in the general method of the analysis to be described. Based as it is upon the processes used by Dr. Squibb for the sampling of the opium and the mode of extraction and precipitation of the morphia, I have attempted to render these still more effective by such modifications as I find necessary in the course of the analysis. The use of the two washing solutions, to be described hereafter, is an important step toward obtaining a pure precipitate of morphia; and the final purification of the crystalline precipitate, proposed by myself, I find to be absolutely necessary for the correctness of the analysis. To this latter point I call special attention. The process of Dr. Squibb, used as he directs, will give results which are almost exactly comparable among themselves. It can be used, therefore, as a control; but to obtain analytical results such as are needed for buying and selling, a still greater degree of accuracy is required. For this purpose I believe the method now to be described to be of great value. It is presented somewhat more in detail than may seem necessary, but I find in my practice that

much of the value of an analytical process depends upon these small and seemingly insignificant points. For the analysis of a substance so complex in its nature as opium, it is necessary that the process used should be simple, easy of manipulation, but yet thoroughly successful in the extraction of all the morphia present. The solvent used and the bulk of the solution obtained should be such that the least possible amount of injury is done to the alkaloid during the course of the analysis.

In Allen's *Commercial Organic Analysis* is found the following account of the

Action of Solvents on Opium.—"The action of different solvents and reagents on opium is shortly as follows:

"Water dissolves meconic acid readily, as also meconate and acetate of morphia; free morphia very sparingly, and narcotine still less so (1 in 1000). Narceine is more soluble than morphine, while the resin, caoutchouc, etc., are insoluble, though certain gummy matters pass into solution.

"Alcohol dissolves free morphia, as well as the acetate and meconate. The other alkaloids of opium, as also the resin and caoutchouc, are dissolved by alcohol.

"Amylic alcohol dissolves all the alkaloids of opium, if in a free state. The resin is also slightly soluble in amylic alcohol.

"Ether, benzene and carbon disulphide dissolve about 0.05 per cent. of free morphia, and the other free alkaloids of opium more readily. These solvents also dissolve the caoutchouc, but not the resin.

"Acids dissolve all the alkaloids from opium, together with the resin.

"Fixed alkalies used in excess dissolve morphine freely, while narcotine remains insoluble. Lime water dissolves morphine, but is a solvent for narcotine only in presence of morphine. The resin of opium is partly soluble in alkalies.

"Ammonia dissolves morphia sparingly, narceine and codeine readily, while the other alkaloids and the resin of opium are insoluble.

"From the foregoing statements, the arrangement of which is mostly due to Mr. E. L. Cleaver,[1] it follows that an aqueous solution of opium will contain meconate of morphine and other alkaloids, calcium salts, meconic acid, extractives, and resinous matter dissolved by the free acid present.

[1] Year-Book of Pharmacy, 1876, p. 502.

"An alcoholic solution will contain, in addition to the above, free narcotine, caoutchouc, fat and resin.

"Opium which has been exhausted with water still retains a bitter taste; but this is probably due to narcotine, as it is removed by carbon disulphide, benzene or ether, in which morphine and its salts are insoluble. If the aqueous solution be distinctly acid, water may be trusted to dissolve the whole of the morphia from opium. In some processes of assaying opium the sample is subjected to a preliminary treatment with benzene or ether to remove narcotine, caoutchouc and coloring matter. By this means the subsequent exhaustion with water is much facilitated and a purer solution of morphine is obtained.

"In presence of much narcotine, morphine is soluble in benzene, but this is not true of the meconate or other *salts* of morphine. Hence there is no loss of morphine on extracting opium with benzene. Meconate of morphia is, however, freely soluble in a mixture of alcohol and chloroform, but the simultaneous presence of ether prevents its solution more or less completely. . . . .

"The ash of opium is readily determined by igniting a weighed quantity of the sample. The residue should not exceed 8 per cent.

"An aqueous solution of opium should give a red coloration with ferric chloride. The production of a black or blue-black coloration or precipitate will be due to tannin, which is not a normal constituent of opium.

"Genuine opium contains no starch, and hence, on boiling with water the residue insoluble in cold water, the solution obtained should give no blue coloration with solution of iodine.

"Sand, stones, bullets and other make-weights are sometimes met with as adulterants of opium. Sugar, gum tragacanth, pulp of apricots and figs, pounded poppy capsules, etc., are also employed for the sophistication of opium."

Of the many processes published for the estimation of morphia in opium, none have proved thoroughly successful and easy of accomplishment. In an article by Dr. E. R. Squibb, published in *Ephemeris*, Jan., 1882, is found a full account of a process used by him, and based upon one published by Prof. Flückiger some two years previous. The reader is referred to the article for the full text of the description, but the essential points are described below. The modifications of the original process introduced by Dr.

Squibb, though slight, have great value, because they lead to a thorough exhaustion of the opium and a better crystallisation of the morphia.

Those analytical processes which depend on the use of lime and on the use of an aliquot portion of the filtrate are unsatisfactory, because they do not thoroughly exhaust the opium; because the discarded portion is richer in morphia than the aliquot portion taken; and, lastly, because the volume of liquid used is too large to allow of the full separation of the morphia. These points were examined by Dr. Squibb, who found in an opium of known strength that the first portion of the solution gave 0.544 gram of morphia, the discarded portion gave 0.595 gram, and the two together did not account for the total amount of morphia present by about one per cent. This loss of morphia was found to be due to the large volume of solution used for the precipitation. A test made by myself on this point gave the following results: 10.18 grams of an opium, which gave, by the process hereafter to be described, 11.76 per cent. morphia, was thoroughly exhausted, and the filtered solution evaporated to 100 cc. The requisite amounts of alcohol, ether and ammonia were added. The precipitate obtained weighed 1.020 grams, equal to 10.00 per cent. The filtrate from the crystals was evaporated to 25 cc. and the requisite amounts of alcohol, ether and ammonia added, and a further precipitate of morphia weighing 0.155 gram was obtained, equal to 1.52 per cent. The total amount found was, therefore, 11.52 per cent. In a pure salt of morphia this effect of dilution is not so important. A crystallised sulphate of morphia, which, if pure, should contain 75.2 per cent. morphia, was dissolved and the morphia crystallised from a total volume of 120 cc. of solution. The crystals obtained equalled a percent. of 74.31. On evaporation of the filtrate to 25 cc., and recrystallisation, 0.20 per cent. more was obtained, giving a total of 74.51 per cent. morphia.

Trials made to test the accuracy of using an aliquot portion of the solution gave results too discordant to be of any service. In one case I obtained 10.63 per cent. instead of 11.76 per cent., the actual amount in the opium.

As regards the accuracy of the process about to be described, the following results may be of interest: A lot of opium, very uneven in quality, was sampled by one of our men, and I made the analysis, obtaining—water, 24.30; morphia, 11.75 per cent. Three

months afterwards the same lot was re-sampled by myself and one of our men, and the resulting sample analysed by me, in duplicate, using different weights of opium for each analysis. The results obtained were—water, 24.70; morphia, 11.70 and 11.82; average, 11.76 per cent. Other results of duplicate tests showing the same agreement might be given if necessary.

Sampling.—The process of sampling and the preparation of the sample are of great importance, as, on account of the varying quality of the lumps of commercial opium, it is very unlikely that any two lumps will be of the same strength. About every tenth lump in a case is sampled by cutting a cone-shaped piece from the middle of the lump, with an ordinary pocket-knife. From the side of this cone a small strip is taken, and the cone returned to its place in the lump. These separate strips are kept in a tin box until the sampling is finished, care being taken that they do not lose moisture by exposure.

Preparation of the Sample for Analysis.—The sample, composed as it is of many small pieces, is treated as follows: A slab of glass or stone about two feet long is provided, though a small board of hard wood will answer. On this the mass of samples is rolled with the hands, until it is worked into a long, thin roll. This is doubled upon itself and rolled again, re-doubled and re-rolled, and so on until a section cut anywhere from the roll shows a perfectly homogeneous surface. The ease with which this is done depends upon the condition of the sample; a moderately dry sample—that is, with 10 to 12 per cent. of water—will roll out very easily without sticking to the hands, while a wetter one will give some trouble; but with care the sample can be made perfectly uniform in so short a time that no loss of moisture will take place. The sample when prepared is wrapped in tin foil, and placed in a suitable box or bottle to be kept for analysis.

If the sample be hard and dry, and cannot be mixed by the above method, break it up coarsely, take an average portion for moisture, and dry in the water bath an average of the remainder, until it is possible to grind it in a mortar to a sufficiently fine powder. Determine the moisture and the morphia in the prepared sample. Then, by calculation, the result is reduced, first, to the amount present on a dry basis, and then to that present in the original sample. If the sample for analysis is powdered opium, no difficulty will occur in getting a fair average sample.

Moisture.—Two separate portions of the average sample, from 6 to 8 grams each, are weighed and dried at 100° C. From samples prepared as above described, duplicates for moisture will agree very closely. For example:

1	24.70	23.13	22.90	20.30	17.90	20.60
2	24.70	23.40	22.70	20.60	17.50	20.70
Average,	24.70	23.26	22.80	20.45	17.70	20.65

Determination of the Morphia.—Weigh off a portion of the average sample, using about 10 grams, noting the exact weight of the portion taken.

"Put the weighed portion into a flask or common wide-mouthed bottle of 120 cc. capacity, fitted with a good cork. Add 100 cc. of water, distilled by preference—but this is essential only when common water contains an unusual amount of inorganic matter—and shake well. Allow it to macerate over night or for twelve hours, with occasional shaking, and then shake well and transfer the magma to a filter of about 10 centimeters = 4 inches diameter, which has been placed in a funnel and well wetted. As it is the shaking which accomplishes the object here in view, rather than the standing, the time of maceration can be easily shortened even to three hours, if the shaking be frequent and active."[1]

Instead of using a flask or bottle I place the weighed portion in a strong beaker, add 100 cc. water, and then, with a glass rod fitted at the end with a piece of thick rubber tubing, I rub and break up the lump of opium, until in a short time it is thoroughly disintegrated. It is best to let the opium stand some hours in order that the morphia be thoroughly extracted. In test assays it was found that if the solution were filtered off as soon as the lump of opium was broken up and no more dark, soft portions were seen, the amount of morphia obtained was less than the actual amount present. Duplicates made in this manner—by filtering as soon as the dark soluble portions were dissolved—did not agree; but by repeating the operation and allowing the opium to digest over night, the duplicates, made with different amounts of opium, agreed exactly in the amount of morphia obtained. The beaker is covered with a watch glass and placed where no ammoniacal vapors will affect it, although, as the water solution is acid from the organic

[1] Ephemeris **1**, 15.

acids present in the opium, no precipitation of morphia will take place until this acidity be neutralised.

I learn from Dr. Squibb that he has lately adopted the plan of adding a few drops of sulphuric acid to the water used for the exhaustion of the opium. The solution is kept slightly acid, and the extraction of the morphia seems to be thereby facilitated.

"As rare exceptions, some powdered opiums will be found which, through natural conditions, give a magma with water which will not filter, or filter so very slowly that the water solvent becomes impracticable. When this is discovered the magma is thrown away and a fresh portion of powder is taken. Wash this by agitation in the bottle with 30 cc. of ether (sp. gr. .728), transfer it to a filter, rinse the bottle with 20 cc. more of ether, and pour this onto the opium in the filter. When this has passed through, wash the filter and opium with 10 cc. more ether applied drop by drop around the edges of the filter and on the surface of the opium. Then dry the powder on the filter and use it as in the case of opium, which does not need to be first washed with ether.

"Opium which is adulterated, or standardised by admixture with dextrine, gums, sugar or glucosides, yields an impracticable magma with water, and ether-washing to such does little or no good. All such samples have to be exhausted with an alcoholic solvent. If not much adulterated a mixture of equal measures of alcohol (sp. gr. 0.820) and water will answer best, but generally a mixture of two measures of alcohol (sp. gr. 0.820) with one measure of water is to be used, instead of water alone, for the exhaustion, and as this mixture is not as good a solvent for the morphia salts in the opium as water, more of it is required, and the washing and percolating should be carried to 250 cc. of solution from the 10 grams of opium. The process after exhaustion is the same as where water is used as the solvent."[1]

Filtering off the Aqueous Solution of Morphia.—Filter off the solution into a graduated cylinder, and wash the filter and residue with water applied from a wash bottle until the filtrate measures about 120 cc.; set this strong solution aside, and return the residue to the bottle or beaker by means of a small spatula; add 30 cc. of water, and mix or shake well, and filter this solution through the same filter. Again return the residue and treat with 20 cc. of

[1] Ephemeris **1**, 15.

water and filter, and finally repeat the treatment with 20 cc. more. By the use of the rubber-tipped rod and a beaker it is possible to so press out the water from the insoluble residue that the above treatment will exhaust 10 grams of any opium. The water is much more thoroughly obtained from the residue than by using several more washings without pressure. It is best to let the several washings stand on the residue for ten minutes or so before transferring to the filter. These washings are received in a beaker, and are the first portion to be evaporated.

Evaporation of the Aqueous Solution of Morphia.—The second portion of the solution, the washings, measuring about 70 cc., is placed in a porcelain capsule of 6 to 8 inches diameter, and evaporated over a water bath at a heat below boiling. By using a broad, shallow dish this evaporation takes little time, and the danger of injury to the alkaloid is reduced to a minimum. Evaporate to about 25 cc. and then add the first portion of the solution, washing out the cylinder with a little water from the wash bottle, and evaporate the whole to about 25 cc. Cool the capsule and contents and add 5 cc. of alcohol (sp. gr. 0.820), and stir until a uniform solution is obtained. If a precipitate is obtained, as sometimes happens, it is not necessary to filter, as this precipitate is removed in a subsequent treatment, and is not reckoned as morphia.

Transferring to the Crystallising Flask.—Pour the solution into an Erlenmeyer flask fitted with a good velvet cork, using a flask of about 2 inches diameter at the bottom and 5 inches high, and wash the capsule with about 5 to 10 cc. of water from the wash bottle. I find that the quantities of water for washing and for the precipitation of the morphia may be slightly greater than those recommended by Dr. Squibb, without injury to the analysis. Add 5 cc. more of alcohol, and mix the liquids thoroughly by rotating the flask, and not by an up and down movement. Then add 30 cc. ether and again mix well by rotating.

"This shaking together first of the watery solution and alcohol causes the alcohol to combine with the water before the ether is added. The ether then added, the second shaking saturates the watery solution and combined alcohol with ether, and then the mixture is ready for the precipitation of the alkaloid under the most favorable condition."[1]

[1] Ephemeris 1, 17.

Precipitation of the Morphia.—Add 4 cc. of ammonia solution of 10 per cent. (sp. gr. 0.960), wet the cork with ether, and insert at once into the flask. Shake the flask *strongly* with an up and down motion until the crystals begin to separate. This will occur in a moment or two if everything has been properly carried out. Then set the flask aside for twelve hours, or over night, to complete the crystallisation. By this vigorous shaking the crystals are obtained in a fine granular condition, easily washed and separated from the flask.

Filtering off the Morphia.—" Pour off the ethereal stratum from the flask as closely as possible onto a tared filter of about 10 centimeters = 4 inches in diameter, well wetted with ether. Add 20 cc. of ether to the contents of the flask, rinse round without shaking, and again pour off the ethereal stratum as closely as possible onto the filter, keeping the funnel covered. When the ethereal solution is nearly all through, wash down the edges and sides of the filter with 5 cc. of ether, and allow the filter to drain with the cover off. Then pour on the remaining contents of the flask, and cover the funnel. When the liquid has nearly all passed through, rinse the flask twice with 5 cc. of water each time, pouring the rinsings with all the crystals that can be loosened onto the filter, and dry the flask in an inverted or horizontal position, and when thoroughly dry, weigh it. Wash the filter and crystals with 10 cc. of water applied drop by drop to the edges of the filter. When drained, remove the filter and contents from the funnel, close the edges of the paper together, and compress it gently between many folds of bibulous paper. Then dry it at 100° C., and weigh it. Remove the crystals of morphia from the filter, brush it off, and re-weigh it to get the tare to be subtracted. The remainder, added to the weight of the crystals in the flask, will give the total yield of morphia, in clean, distinct, small, light brown crystals.

" Take a small portion of these crystals, rub them into very fine powder, and weigh off 0.1 gram. Put this in a large test tube fitted with a good cork, and add 10 cc. of officinal lime water. Shake occasionally, when the whole of the powder should dissolve. (Absence of Narcotine: Flückiger.)

" . . . This process, according to the skill and care with which it is managed, will give uniform results to within two or three-tenths of a percent. Adulterated opiums are much more difficult to assay, and yield crystals which are always darker and less clean, and

therefore the results are almost always too high. Poor opiums, on the other hand, are very easy to assay, and usually give very light-colored, clean morphia. The results here are liable to be too low, because, when the quantity of morphia is small, the alcohol and ammonia used are proportionally too large, so that much morphia may be retained in the mother-liquor. Therefore, when the morphia comes out very white and in small proportion, the assay should always be repeated, evaporating the solution to 10 grams instead of 20, and adding 5 cc. of alcohol instead of 10, and 2.5 or 3 cc. of ammonia instead of 4. . . .

"The above process is very easily applicable to the assay of such preparations of opium as the tincture, deodorised tincture and compound solution. For the assay of these:

"Take of the liquid preparation 120 cc. Evaporate at a low temperature to 10 grams, and from this point proceed exactly as in the above process, using, however, 5 cc. of alcohol instead of 10, and 2.5 to 3 cc. of ammonia instead of 4."[1]

In following out the above plan of Dr. Squibb, several difficulties are met with. The amount of ether recommended for washing is so small that in some cases where the operation of filtering proceeds with great difficulty, much of the ethereal solution is evaporated from the edges of the filter paper, leaving its contents behind, and these are not thoroughly washed out by the subsequent treatment. The amount of water, also, is too small to allow of perfect washing.

Washing Solutions.—In order to obviate these difficulties I have adopted a plan for which I am indebted to a paper published by E. F. Teschemacher, F. C. S., etc., in the *Chemical News*, Vol. 35, p. 47. The first solution, which he calls "*Morphiated Spirit*," is made by mixing one part of ammonia solution, sp. gr. 0.880, with twenty parts of alcohol, and digesting in this mixture, for several days, a large excess of morphia. The clear solution will contain 0.33 per cent. of morphia. The second solution, called "*Morphiated Water*," is water saturated by long shaking with morphia. The filtered solution contains 0.04 per cent. morphia.

By washing with these solutions the extractive matter is completely removed from the filter paper and crystals of morphia. I prefer to use balanced filter papers, of 4½ inches diameter. The solution is run through one of these, and, by means of the thorough

[1] Ephemeris **1**, 17, 20.

washing with the solutions above described, the two papers are left, at the end of the operation, ready for weighing against each other as at first. I pour off the ethereal stratum through the filter as above described, and then wash several times with 10 cc. of ether, rinsing the flask around without shaking, and letting settle for a few minutes. Even if a small amount of the ethereal residue is left upon the paper by evaporation, it is immaterial, as in the subsequent treatment this is removed. A small syphon is advantageously used to draw off the ethereal solution from the Erlenmeyer flask, but if an attempt be made to syphon off the ethereal washings, it will be found that the bubbles formed in the ether collect in the tube of the syphon and prevent its action, so that it is better to wash by decantation. If some of the aqueous solution pass onto the filter with the ether, it is of no importance. The washing with ether is followed, first, by a thorough washing with the "*Morphiated Spirit*," thus removing all the coloring matter and resin soluble in this menstruum, and then by a thorough washing with the "*Morphiated Water*," until the filtrate comes through colorless and the paper shows by its color that all the extractive matter is removed. By the use of the Erlenmeyer flask it is possible to remove with the rubber-tipped rod all the crystals from the flask, so that no drying and weighing of the flask is needed. After the washing with the "*Morphiated Water*" the filter is left to drain for a few minutes in the funnel, and two washings of 10 cc. each with the "*Morphiated Spirit*" are given. This removes the bulk of the water from the paper and crystals. Let drain for a few minutes, keeping the funnel covered with a watch glass, and then wash twice with 10 cc. each time of ether. This will remove any narcotine which may have been left from the evaporation of the ethereal solution at the beginning of the operation. The paper and contents are thus left in a condition to be rapidly dried. Let the filter and its contents stand exposed for a few minutes, and then dry it at 100° C. and weigh. Twenty minutes or half an hour's drying is usually sufficient.

On account of the removal of the water it is possible to dry the filter and its contents in a short time at a much lower temperature than 100° C., but as it is easier to employ this heat, and no decomposition of the morphia crystals occurs, I use it. A precipitate of morphia crystals was dried for two hours at 60° C., yielding a weight of 1.306 grams. It was further dried for three hours at the

same heat, and then weighed 1.305 grams; still further dried for two hours at 100° C., it became 1.301 grams.

The mother-liquor, together with the first washings of ether and "*Morphiated Spirit*," is put in a flask, 3 cc. of ammonia added, and the corked flask is set aside over night in order to see if a further crystalline precipitate of morphia occur. If the solution is left exposed in an open beaker, amorphous flakes will settle out, consisting chiefly of resinous matter, very different from the heavy crystalline deposit of morphia.

Having thus obtained the weight of the crystalline precipitate, it is still necessary to further purify it before the final calculation is made for the percent. The precipitate of morphia obtained by Dr. Squibb's process contains insoluble matter, resinous and other organic matters soluble in alcohol, and meconate of lime, the latter constituting about 25 per cent. of the impurities present. The average amount of the impurities present in the crystals obtained by his process is 8 per cent. of the weight of the crystals. The meconate of lime extracted by the acid solution of the opium is retained in solution until the addition of the ammonia, when it is precipitated with the crystals of morphia, and remains with them until the final weighing. The resinous and other organic matters, insoluble in water, but soluble in alcohol, are not thoroughly removed with the limited washing given in his process, and no provision is made for their subsequent removal. The thorough washing with "*Morphiated Spirit*" which I employ takes out these substances, and the subsequent treatment with "*Morphiated Water*" removes those insoluble in alcohol, so that the chief impurity present in the crystals of morphia obtained by my modification of the process is meconate of lime, together with some organic matters insoluble in water and alcohol.

Purification of the Precipitate.—After drying and weighing the crystals they are carefully rubbed or brushed from the filter, the latter being then placed in a funnel and preserved with its balanced paper for future use. The precipitate is treated in a small beaker with hot alcohol of 95 per cent. This dissolves all the morphia, leaving the insoluble organic matter and meconate of lime. The hot alcoholic solution is run through the filter which contained the morphia, the small portion of the crystals remaining on the paper being thus drenched with hot alcohol and the morphia dissolved. This treatment with hot alcohol is continued until all the morphia

is dissolved. This extraction with alcohol may be done in a Soxhlet's apparatus, if desired. The filter is then dried with its balanced paper and the amount of residue obtained. This is subtracted from the original weight of the precipitate, and the remainder calculated into the percent. of morphia. The alcoholic solutions of morphia are placed in a bottle and left to deposit the excess of morphia, and the alcohol, saturated with morphia, is used for the preparation of the "*Morphiated Spirit*" as before described. Meconate of lime I found to be perfectly insoluble in boiling alcohol. A long treatment with this solvent failed to dissolve enough meconate of lime to give a trace of color with ferric salts.

The composition of the morphia crystals, on which the calculation for the percent. is based, is $C_{34}H_{19}NO_6 + 2Aq$, containing 5.94 per cent. of water of crystallisation. At 120° C. the water is expelled, and at a higher temperature the crystals become carbonised.

The following is a brief summary of my process as practised in our laboratory.

1. *Sampling.*—By taking a portion of every tenth lump in a case.

2. *Preparation of the Sample.*—By thorough mixing of the small samples obtained, either by kneading and rolling, or by drying the sample, with previous estimation of the water.

3. *Extraction of the Morphia.*—Weigh off about 10 grams, noting the exact weight taken; treat with 100 cc. of water in a suitable vessel, macerate, let stand over night, filter and wash, making two portions of the filtrate. Evaporate on a water bath, first the weaker portion, about 70 cc. of solution, then add the stronger portion, and evaporate all to 25 cc.; add 5 cc. of alcohol and stir until all is dissolved.

4. *Precipitation of the Morphia.*—Transfer the solution to a suitable flask, add 5 cc. more of alcohol, mix; then add 30 cc. of ether, mix; then add 4 cc. of a 10 per cent. solution of ammonia, sp. gr. 0.960. Shake violently until the crystals form, and let stand over night.

5. *Filtration of the Morphia.*—Filter off, first, the ethereal solution and wash well with ether. Then filter the aqueous solution, and wash, first with "*Morphiated Spirit,*" then with "*Morphiated Water,*" then with "*Morphiated Spirit,*" and finally with ether. Dry at 100° C. and weigh, using balanced papers.

6. *Purification of the Morphia.*—Treat the impure precipitate

with hot alcohol until all the morphia is dissolved, wash thoroughly with hot alcohol, dry and weigh the insoluble residue. Subtract this from the first weight of the precipitate to get the amount of morphia present.

7. *Statement of the Result.*—Give the percentage of moisture present at 100° C., and of morphia, both on a wet and a dry basis, in terms of crystallised morphia, $C_{34}H_{19}NO_6 + 2Aq$, dried at 100° C.

Washing Solutions.

a. "*Morphiated Spirit.*"—This is made by mixing one part of ammonia solution, sp. gr. 0.880, with twenty parts of alcohol and saturating with morphia. The filtered solution contains 0.33 per cent. of morphia.

b. "*Morphiated Water.*"—This is made by saturating water by long shaking with excess of morphia. The filtered solution contains 0.04 per cent. of morphia.

c. Ether.—Called stronger ether, sp. gr. 0.728 at 15.5° C.

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ON THE ACTION OF CHLORINE UPON PYRIDINE.

[PRELIMINARY COMMUNICATION.]

By E. H. Keiser.

The action of the halogen elements upon the bases of the pyridine series has been but little studied, and our knowledge of the halogen derivatives of these bases is very imperfect. This is undoubtedly due to the fact that pyridine is one of the most stable of organic compounds, and its substitution products can only be obtained with the very greatest difficulty. The first work in this direction was undertaken by Anderson[1] in 1857. Having succeeded in isolating a quantity of pyridine from the bases which accompany it in bone oil, he endeavored to throw some light upon its constitu-

[1] Liebig's Annalen der Chemie **105**, 340.

tion by studying its decomposition products. He tried, in the first place, the effect of oxidising agents upon pyridine, but found that it remained undecomposed when boiled with concentrated nitric acid, and that even a boiling solution of chromic acid produced no change. He then studied the action of the halogens upon pyridine, but found that in this way no definite results could be obtained. In regard to the action of chlorine upon pyridine, he observed that when a current of this gas is conducted into an aqueous solution of pyridine, the chlorine is rapidly absorbed; the solution becomes dark brown in color, and acquires a peculiar irritating odor. If caustic potash be thereupon added to the liquid, a dark brown resin is formed and the solution again has the odor of pyridine. He also noticed that if an excess of pyridine be poured into a large vessel containing chlorine, and if the pyridine be rapidly distributed upon the walls of the vessel to avoid an increase of temperature, then it does not become dark brown in color, but is converted into a mass of radiating crystals. These crystals dissolved readily in water, but at the same time a small quantity of a snow-white powder remained undissolved. When dried, the white powder had an odor resembling that of bleaching powder. None of the substances obtained by Anderson were analysed, and, therefore, no information was obtained in regard to the constitution of pyridine. He also treated pyridine with bromine and iodine, but in these cases the results were not more satisfactory than in the case of chlorine.

From an examination of the literature on this subject it appears that since these experiments of Anderson no other attempts have been made to study the action of chlorine upon pyridine. Two chlorine derivatives[1] of pyridine have been described, but these have been obtained by indirect methods, and not by the direct action of chlorine upon pyridine.

Hofmann[2] has studied the action of bromine upon pyridine, and found that an orange-yellow crystalline addition product is formed when a hydrochloric acid solution of the base is treated with bromine. The addition product is unstable, being decomposed when heated. It probably has the formula $C_5H_5NBr_8$. If this crystalline addition product be heated to a temperature of 200° in sealed glass tubes, some bibrompyridine, $C_5H_3Br_2N$, is formed.

[1] Berichte der deutschen chemischen Gesellschaft **14**, 1154; **15**, 1179; **17**, 594.
[2] *Ibid.* **12**, 990.

Hofmann also found that bibrompyridine is formed by heating pyridine hydrochlorate with bromine in sealed tubes, in the proportion of one molecule of pyridine hydrochlorate to two molecules of bromine.

The present investigation was undertaken with the intention of studying more thoroughly the action of the halogen elements upon the bases of the pyridine series. The object was to determine the conditions under which addition and substitution products may be formed, and by a study of these derivatives to throw some light upon the constitution of the bases themselves. The investigation began with the study of the action of chlorine upon pyridine. Preliminary experiments soon showed that when chlorine comes in contact with an aqueous solution of pyridine the effect is totally different from that which is produced when chlorine acts upon pure pyridine.

If a current of dry chlorine be conducted into a vessel containing pyridine, which is free from water, the gas is rapidly absorbed and heat is evolved. The pyridine soon becomes yellow in color, then red, and afterwards dark red. Crystals then begin to separate, and finally, if the supply of chlorine is continued, the liquid will be completely converted into a brownish-black solid mass. This black solid is very deliquescent in the air. It dissolves readily in water and alcohol; but it is insoluble in ether, benzene and acetone. The black solid was heated in a retort; it melted below 100°, and on raising the temperature an oily liquid distilled over at 116°. The heating was continued, and at 130° a white crystalline solid condensed in the neck of the retort. These crystals were removed, and on heating still higher the contents of the retort bumped violently; nevertheless a considerable quantity of a yellow waxy solid condensed in the receiver.

An examination of the distillation products showed that the liquid which came over at 116° was unchanged pyridine. It contained in solution some of the crystalline solid which distilled at 130°. This was separated by diluting the pyridine with a large quantity of water. On standing, the solution contained a quantity of crystalline needles. The crystals thus obtained, as well as those which condensed in the neck of the retort, were purified by repeated recrystallisation from alcohol. When pure, they present the appearance of long, slender white needles, which melt at 72°. They dissolve readily in pyridine and alcohol, but are insoluble in

water. The substance is very stable in the air; it does not deliquesce, and has an agreeable aromatic odor. To determine the nature of this derivative of pyridine a portion was dissolved in alcohol, and the solution was treated with platinum tetrachloride. A beautiful, yellow, crystalline double salt was obtained, which differs very much in appearance from pyridine platinum tetrachloride. An analysis of the salt showed that it corresponded in composition with the double salt of a bichlorpyridine.

.1054 gram of the salt gave .0291 gram metallic platinum = 27.60 per cent.

$(C_5H_3Cl_2NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	27.61	27.60

It seemed, therefore, highly probable that the crystalline substance was the hydrochlorate of bichlorpyridine, and a determination of chlorine confirmed this view.

.1370 gram substance gave .3154 gram AgCl = 56.93 per cent. chlorine.

$C_5H_3Cl_2NHCl$.	Calculated.	Found.
Cl	57.6	56.93

The quantity of substance obtained was so small, however, that, after the preceding experiments had been made, there was not sufficient material remaining for making a combustion of the compound. I shall endeavor to prepare it in larger quantity, and hope to be able to study it more thoroughly.

The yellow waxy solid, which was obtained as the last distillation product from the black mass, was purified by redistillation. It boiled at 218°, and the larger quantity passed over at 219°. It can not be distilled without decomposition, and after each distillation a quantity of carbon remained in the retort. The vapor of the compound attacks and destroys cork. The solid substance is extremely deliquescent in the air, and dissolves readily in alcohol. To determine whether it was an addition or substitution product of pyridine, a portion was dissolved in water, and the solution was treated with platinum tetrachloride. A red crystalline double salt was obtained, which possessed all the properties of pyridine platinum chloride.

.1401 gram salt gave .0475 gram metallic platinum.

$(C_5H_5NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	34.31	33.95

It appeared, therefore, that the waxy, deliquescent solid was an addition product of chlorine and pyridine. An analysis of the compound gave the following result:

I. .2691 gram substance gave .5131 gram CO_2 and .1223 gram H_2O = 52.0 per cent. C and 4.68 per cent. H.

II. .0965 gram substance gave .1206 gram AgCl = 30.89 per cent. Cl.

These results indicate that the addition product has a composition which may be represented by the formula C_5H_5NCl.

	C_5H_5NCl.	Calculated.	Found.
C	59.85	52.39	52.00
H	5.00	4.37	4.68
N	14.01	12.28	...
Cl	35.37	30.96	30.89
	114.23	100.00	

A determination of the vapor density of the compound was made at a temperature of 250°. The specific gravity was found to be 2.49, a result which indicated that at that temperature the compound had suffered dissociation.

Briefly stated, the results obtained are as follows: When dry chlorine gas acts upon pyridine the gas is rapidly absorbed, heat is evolved, and the liquid is converted into a black solid mass. This black solid consists chiefly of an addition product of chlorine and pyridine, whose composition may be represented by the formula C_5H_5NCl. There is also present in the black solid some unchanged pyridine and a small quantity of bichlorpyridine hydrochlorate, $C_5H_3Cl_2NHCl$. The latter substance crystallises in beautiful needle-shaped crystals, and is a very stable compound.

If, however, the pyridine is diluted with water and chlorine allowed to pass through the solution, then the action is totally different from that which has just been described.

Twenty cubic centimeters of pyridine were diluted with an equal quantity of water, and a current of chlorine was passed into the solution. The gas was rapidly absorbed, the liquid became warm and soon acquired a dark red color. After a time small bubbles of gas were evolved from all parts of the liquid, and this evolution of gas increased and continued for a long time after the current of chlorine had ceased. An examination of the gas showed that it consisted of a mixture of nitrogen and carbon

dioxide. The solution of pyridine was then diluted with water, and a small quantity of a snow-white, flocculent precipitate was obtained. It was removed by filtration; and, after drying, it was found to have an odor resembling that of bleaching powder. A further examination of its properties showed it to be identical with the white powder obtained by Anderson.[1] A qualitative test showed that the white powder contained nitrogen. The alcoholic solution of the white substance was treated with platinum tetrachloride, and a dark red, crystalline, platinum double salt was obtained. After purification this salt resembled in its properties the double salt of pyridine and platinum tetrachloride.

When analysed .1132 gram of the salt gave .0388 gram metallic platinum = 34.28 per cent.

$(C_5H_5NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	34.31	34.28

The white substance must therefore be an addition product of pyridine. From its method of formation, and its unstable character, it seems probable that the substance is a hypochlorite of pyridine, C_5H_5NHOCl. The composition of this white substance will be studied more thoroughly in a future investigation.

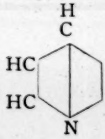
It seems probable, then, that when chlorine is passed into an aqueous solution of pyridine, pyridine hypochlorite is formed, and the evolution of nitrogen and carbon dioxide is due to the decomposition of this compound. Experiments were made with alkaline hypochlorites and aqueous solutions of pyridine. It was found, in every case, that, whenever pyridine was heated with solutions of hypochlorites, nitrogen gas was evolved. Under certain conditions this decomposition of pyridine by hypochlorites took place very rapidly. In one experiment 50 grams of caustic potash and 5 grams of pyridine were dissolved in 300 cc. of water, and chlorine was passed into the solution. In a short time decomposition began, and, as the current of chlorine was not instantly stopped, the evolution of nitrogen became so rapid that the larger portion of the liquid was thrown violently out of the flask. In another experiment, which was made with the same quantity of materials, the nitrogen was evolved with explosive violence, and the flask containing the solution was shattered. If the temperature of the flask containing the solution of pyridine and alkali is kept down by surrounding it with cold water, the decomposition takes place

[1] Liebig's Annalen der Chemie **105**, 340.

slowly, and the nitrogen gas is evolved much more regularly. Several grams of pyridine were decomposed in this way, and an examination of the liquid showed that the decomposition products, beside the nitrogen and carbon dioxide, were chloroform and chloracetic acid. The chloroform was removed from the liquid by distillation. It was recognised in the distillate by its odor, by its reducing action upon Fehling's solution, and by its formation of isocyanphenyl with aniline and alcoholic potassa. The liquid, from which the chloroform had been removed, was evaporated to dryness and extracted with absolute alcohol. The alcoholic solution was treated with silver nitrate, and, on standing, a salt separated which blackened in the light. Although it was too impure for analysis, it possessed all the properties of silver dichloracetate. When heated on platinum foil the salt deflagrates, and with alcohol and sulphuric acid the ethyl ester is obtained, which may be readily recognised by its pleasant odor.

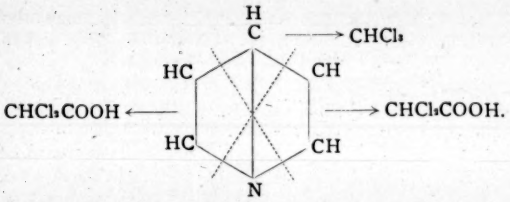
As a result of these experiments it appears, therefore, that when pyridine is decomposed in an aqueous solution by chlorine, or by hypochlorites, there are formed, beside nitrogen and some carbon dioxide, chloroform and dichloracetic acid.

While in recent years pyridine and pyridine derivatives have been built up synthetically from simpler substances, no experiments have hitherto been described in which the pyridine molecule has been decomposed into simpler organic compounds. The fact that chloroform, chloracetic acid and nitrogen are so easily obtained as the decomposition products of pyridine may perhaps be regarded as a confirmation of the hypothesis of Riedel[1] in regard to the constitution of the pyridine molecule. If we assume the formula

of pyridine to be 

, then it is not difficult to account for the formation of chloroform and chloracetic acid, for it may be supposed that decomposition takes place as is indicated by the dotted lines.

[1] Berichte der deutschen chem. Gesellschaft **16**, 1609.



If, however, we assume Körner's ring formula as representing the constitution of pyridine, then we would naturally expect to find much more complicated decomposition products—that is, compounds which contain more than two carbon atoms.

This investigation will be continued in the directions indicated, and will include a study of the action of the halogen elements upon the other members of the pyridine series of bases.

BRYN MAWR, PA., *August*, 1886.

ABSORPTION TUBES FOR THE ESTIMATION OF CARBONIC ACID IN ATMOSPHERIC OR GROUND AIR.

BY THOMAS C. VAN NÜYS.

Having employed Pettenkoffer's absorption tubes[1] in connection with an apparatus, described and illustrated in this Journal, Vol. 8, No. 3, in estimating carbonic acid in the air, I found that the Pettenkoffer tubes yielded results too high and subject to greater variation than those obtained with my apparatus. This I concluded was due to the absorption of carbon dioxide from the air by the baryta after a measured quantity of air had passed through the tubes and before titrating with the oxalic acid solution. To overcome this difficulty I devised the tubes represented in Fig. 1. They were made by Mr. Emil Greiner, 79 Nassau st., New York.

[1] Annalen der Chemie, Suppl. Bd. 2, 93; Zeitschrift für analyt. Chemie 1, 495.

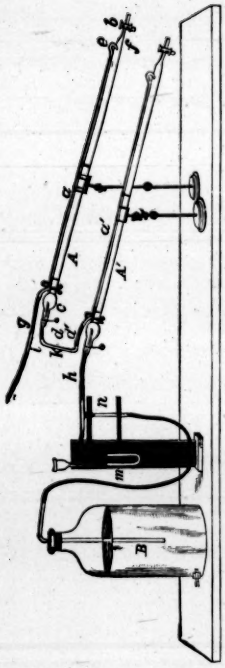


FIG. 1.

As each tube is of the same construction, the description of one will answer for both.

Tube *A* from the stop-cock *b* to the bulb *c* is 90 cm. in length, and its external diameter is 16 mm. and internal diameter about 11 mm. The outside diameter of the enlarged portion or bulb *c* is 4 cm. The capacity of the tube from the stop-cock to the bulb is 96 cc. The stopper *d* fits with a ground surface in the tube, and is drawn out at either end. A rubber tube fits over the distal end, and the other end is bent and drawn out to a certain extent. This extremity of the stopper is therefore directed towards the upper part of the surface of the enlarged portion of the tube. Passing through the stopper longitudinally is an opening 4 mm. in diameter, except at its proximal extremity, where the diameter is about 2 mm. The small tube *a* is fastened to the absorption tube by having rubber tubing placed over it in two places and secured by fine cord. Its outside diameter is 6 mm. Within a few centimetres of the stop-cock the tube, after making the curve *e*, enters the absorption tube and is welded with the latter at point of entrance.

In the absorption tube it is drawn out and somewhat curved in its course, so that its extremity *f* is directed towards the centre of the absorption tube. The diameter of the orifice of the tube at *f* is less than 1 mm. At the enlarged portion of the absorption tube the small tube *a* is bent, and terminates nearly opposite and about 5 cm. from the stopper. The aspirator bottle *B* is connected with the absorption tube *A'* by tubing. The manometer *m* communicates with the absorption tube and aspirator bottle by means of

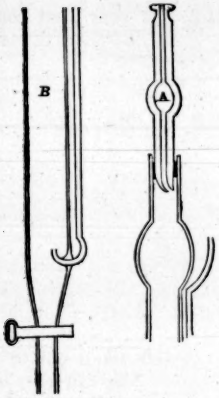


FIG. 2.

the T tube *n*. The construction of the stopper of each absorption tube and the tube *a* or *a'* (Fig. 1) as it terminates in the absorption tube are illustrated in Fig. 2.

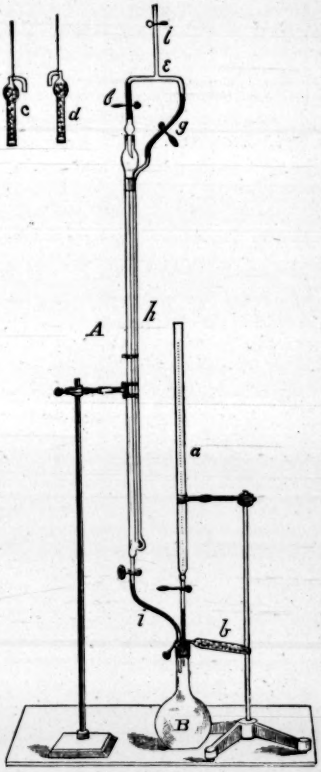


FIG. 3.

Fig. 3 represents one of the absorption tubes connected with the flask *B*. The flask is provided with a rubber stopper having three holes, through one of which a bent glass tube passes, which is connected with the absorption tube by means of a rubber tube. The long tip of the burette *a* passes through the second hole, and through the third hole the bent end of the calcium chloride tube *b* passes. This tube is filled with pumice saturated with a strong solution of sodium hydrate. The calcium chloride tubes *c*

and *d* contain soda-lime. The lower end of each tube is closed with a cork stopper having a small perforation, and the soda-lime is secured in place by some cotton in either end. The rubber tube *j*, connected with an aspirator bottle containing water about one metre above the upper end of the absorption tube, is attached to the T tube *e*. Besides showing the plan of the absorption tubes, Fig. 1 illustrates their position and relation to each other when they are being filled with air free of CO_2, and when the process of absorbing the carbonic acid of the air is in progress.

By Fig. 3 the processes of filling, emptying and washing them are illustrated.

The barium hydrate solution I use is made by dissolving about 3.5 grams in 1000 cc. water, and to this solution about 2 grams barium chloride is added to react on any potassium or sodium hydrate that may be present as an impurity. If the solution formed is not clear it should be filtered into a tubulated or aspirator bottle, which, to prevent the ingress of air containing carbon dioxide, is provided with a rubber stopper with which a simple calcium chloride tube is fitted with its drawn-out extremity bent, and the tube filled with pumice saturated with a strong solution of sodium hydrate. The oxalic acid solution used is prepared by dissolving 2.8636 grams pure acid in 1000 cc. water. Solution of oxalic acid of this strength was first employed by Pettenkoffer; 1 cc. of it equals the saturating power of 1 milligram, or 0.5084 cc. carbon dioxide at normal temperature and pressure. To ascertain how much of the oxalic acid solution is required to neutralise 50 cc. of the barium solution, the titrations should be carried on in the absence of air containing carbon dioxide.

To accomplish this the method of F. Schulze[1] may be employed. Into a 100 cc. flask, having been cleaned and dried, a piece of sodium hydrate is suspended by means of a wire. The flask is closed by a stopper, allowed to stand a few hours, when the sodium hydrate is carefully drawn out. A piece of rubber sheet having a small perforation is placed over the mouth of the flask and secured by a rubber band, and into the flask through the small opening in the rubber sheet a few drops of an alcoholic solution of rosolic acid are introduced by means of a small pipette, after which 50 cc. of the baryta solution are introduced from a pipette which has been filled by Pettenkoffer's method, when the tip of a 25 cc. burette

[1] Zeitschrift für analyt. Chemie 9, 292.

containing the oxalic acid solution is introduced through the perforation, and the solution is titrated until the red color of the rosolic acid disappears.

With as great security against the presence of carbonic acid, the flask in Fig. 3 may be employed by having been dried, two or three drops rosolic acid solution introduced, the bent glass tube pushed further down into the flask, the rubber tube attached to a wash bottle containing a strong solution of sodium hydrate, and a U-shaped calcium chloride tube containing soda-lime and cotton, the latter next the flask, and through these the air is drawn into the flask by attaching the end of the calcium chloride tube *b* to an aspirator. When three or four litres of air have been drawn through, the rubber tube is secured by the pinch-cock. Into the free end of the tube filled with water the tip of a 50 cc. pipette filled with the barium solution is introduced, and by loosening the pinch-cock the solution is let into the flask. Some water is introduced in the same way, so as to wash all of the barium solution from the tube, when the solution is titrated with the oxalic acid solution in the burette. When an agreement is reached it is found that from 23.5 to 24 cc. oxalic acid equal 50 cc. of the barium hydrate solution. Both absorption tubes are so connected that when the tube *g* (Fig. 1) is attached to a wash bottle containing a solution of sodium hydrate, and two U-shaped calcium chloride tubes containing soda-lime, and some cotton in the tube next to tube *g*, the absorption tubes can readily be filled with air free of carbon dioxide, but the air should not be drawn through with great rapidity, and the cotton should be in quantity sufficient to arrest any particles of soda-lime that may be separated by the air.

The absorption tubes having been filled with air free of carbon dioxide, the rubber tubes *gi* and *jh* are secured by pinch-cocks. Each absorption tube is filled with the barium hydrate solution, by placing them in position as in Fig. 3. The rubber tube *f* is placed over the bent end of either tube *c* or *d*. The tip of a 50 cc. pipette filled to the mark with the barium solution is introduced into the rubber tube *g*, when the pinch-cocks are removed from the tubes *g* and *f*, and the solution will run through the small tube *h* into the absorption tube, after which from 30 to 35 cc. water are introduced in the same way, when the rubber tube *g* is secured by the pinch-cock; and that the water may pass down from the end of this tube, connection is made with it and tube *d*, when the water will descend

by loosening the pinch-cock. Both tubes having been secured by pinch-cocks, the absorption tube is ready for use. The other absorption tube is filled in the same way, and they are connected as before by means of the glass tube *k* (Fig. 1). The tube *l*, through which air passes to enter the absorption tubes, is two or three metres long. It cannot well be dispensed with, as there is great liability of the air becoming charged with an increased quantity of carbonic acid by persons remaining any length of time about the apparatus while air is passing through the tubes. I found this true in several instances. For the same reason the apparatus is placed so that the movement of air, if appreciable, is from the open end of the tube *l* towards the apparatus.

Before passing air through the absorption tubes all rubber tubing making connections is secured by fine iron wire, and to ascertain if the connections are air-tight, all of the pinch-cocks, except the one securing tube *g*, are removed, and by turning the stop-cock of the aspirator bottle, if air ceases to pass through the absorption tubes, and especially after closing the stop-cock of the aspirator, the mercury in the manometer remains stationary, the connections are air-tight. When the pinch-cock securing the tube *g* is opened so that air may enter, it passes through both absorption tubes, and enters the aspirator bottle as the water escapes. By measurement of the latter, taking into account the pressure and temperature, the quantity of air at 0° C. and normal pressure which passed through the tubes is ascertained.

The pinch-cock securing the tube *g* is gradually opened by means of a metallic wedge, so that air may pass through the absorption tube *A* in small bubbles. If they tend to unite to any great extent, or the current is interrupted, the pinch-cock is adjusted so that less air may enter. It will be found necessary to adjust the pinch-cock on the tube in the same way, employing a metallic wedge or a pinch-cock provided with a screw, so as to regulate the size of the bubbles in the absorption tube *A'*. If the operator trust to the adjustment of the stop-cock of the aspirator bottle, liability to failure in securing a correct result is very great, as the air bubbles formed are often large, and some carbonic acid may escape absorption. By passing air through the tubes at the rate of three litres per hour, all of the carbonic acid is absorbed. In nearly all of the estimations made with these tubes eight litres of air were passed through the tubes, requiring

about two and a half hours. The temperature of the air, the height of the barometer and of the mercury in the manometer do not receive special attention until near the end of the process, for the reason that should there be changes in temperature or pressure the current of air through the tubes and the flow of water are so regulated that the volume of air in the aspirator bottle at the expiration of two, three or four hours corresponds to the volume of water which had escaped the last moment of the process.

For example, at the expiration of two hours the temperature was 8° C., when four litres of air had entered the aspirator bottle; but at the expiration of the fourth hour the temperature was 12° C., the barometric pressure remaining the same. During the last two hours 4000 cc. air in the aspirator expanded $\frac{4}{273}$ of its volume. $4000 \times \frac{4}{273} = 58.6$. The increase of 58.6 cc. due to expansion by increase of temperature during the process prevented an equal volume of air from entering the aspirator bottle, consequently 58.6 cc. water passed out of the aspirator bottle and was measured, while no air passed through the absorption tubes to supply the place.

In the reduction of the volume of air to normal temperature, taking into account the increased temperature as ascertained at the end of the process, the correction is made. It is at once perceived that if the temperature were reduced during the process, a greater volume of air would pass through the absorption tubes than that occupied by the water from the aspirator bottle. For the same reason, to avoid incorrect results arising from change of temperature or barometric pressure during the process, the aspirator bottle is filled to the stopper. In case the aspirator contained air at the beginning of the process, and a change of temperature or pressure took place during the process, the volume of water measured does not represent the volume of air passed through the tubes at the temperature and pressure at the end of the process without taking into account the expansion or contraction of the air in the aspirator at the beginning of the process. As temperature is a very important factor to be taken into consideration in reaching correct results, the water in the aspirator, before beginning the process, should be about the temperature of the air, and the apparatus is placed so as to be protected from the direct light of the sun, to avoid difference of temperature of the air and water in the aspirator at the end of the process. Preparatory to emptying and washing the

tubes the 50 cc. burette *a* (Fig. 3) is filled with the oxalic acid solution. Two or three drops of an alcoholic solution of rosolic acid are introduced into the flask *B*, and it is filled with air free of carbonic acid as above, when the rubber tube *i* is closed by means of the pinch-cock, and its end is filled with water, as well as the glass tube from the glass stop-cock of the absorption tube. The end of the rubber tube is fitted over the glass tube. In this way no air containing carbonic acid can enter the flask. The end of the rubber tube *f* is filled with water from the pinch-cock and fitted over the bent extremity of either *c* or *d*, and the pinch-cock is removed. The glass stop-cock of the absorption tube is turned gradually so that the fluid in the tube passes slowly into the flask, and, when empty, the tube *f* is again closed by means of the pinch-cock, and the calcium chloride tube disconnected.

The ends of the T tube *e* are loosely introduced into tubes *f* and *g*, and the pinch-cock securing tube *j* opened to a certain extent, so that the T tube and the ends of the rubber tubes become filled with water, to the exclusion of air. To this end the internal diameter of the T tube should not exceed 3 mm. The pinch-cock is removed from tube *j*, and the pinch-cocks closing tubes *f* and *g* are alternately opened and closed, and the stopper turned so that a stream of water is directed against different parts of the bulb of the absorption tube. With some practice 75 cc. water will wash every trace of the barium solution into the flask.

The tube *i* is closed with the pinch-cock, and the fluid of the other absorption tube is emptied into the flask in the same way. It is not necessary that the barium solution and wash water from both tubes exceed 250 cc. When the second tube is emptied and washed the tube *i* is closed with the pinch-cock, the absorption tube disconnected, and the barium solution in the flask is titrated with the oxalic acid solution in the burette.

That the processes of filling, emptying and washing these tubes are carried on without the introduction of air containing carbonic acid was proved by omitting the passing of air through the tubes, otherwise carrying on the processes as above, and arriving at the same results as by use of the flask as above in standardising the barium hydrate solution. The tubes can be filled with air free of carbon dioxide and charged with the barium solution and the process begun in thirty minutes, and in the same length of time the tubes can be emptied, washed and the titration made.

The following are the data of one estimation of carbonic acid in the air:

47.9 cc. oxalic acid solution equal 100 cc. of the barium hydrate solution.

Process of absorption from 9 A. M. to 11.40 A. M.

Air passed, 8195 cc.

Thermometer reading at end of process, 20° C.

Barometer reading at end of process, 745 mm.

Manometer reading at end of process, 43 mm.

Vapor tension at 20° C., 17 mm.

$$\underset{\text{Man.}}{43 \text{ mm.}} + \underset{\text{V. tension.}}{17 \text{ mm.}} = 60 \text{ mm.}$$

$$\underset{\text{Bar.}}{745 \text{ mm.}} - 60 \text{ mm.} = 685 \text{ mm.}$$

Volume of air at normal pressure (760 mm.) and normal temperature (0° C.) $= \frac{273}{293} . 8195 . \frac{685}{760} = 6882$ cc.

In titrating, 44.29 cc. oxalic acid solution were required to neutralise the barium hydrate solution; consequently, with the barium solution the equivalent of 3.61 cc. of the oxalic acid solution is combined with the carbonic acid.

As 1 cc. of the oxalic acid solution corresponds to 0.5084 cc. CO_2 at normal temperature and pressure, there is carbonic acid found, $0.5084 \times 3.61 = 1.835324$ cc., therefore in 10,000 vols. air there are $6882 : 1.835324 :: 10{,}000 : 2.66$ vols.

INDIANA UNIVERSITY LABORATORY, BLOOMINGTON, INDIANA.

Contributions from the Agricultural Experiment Station of the University of Wisconsin.

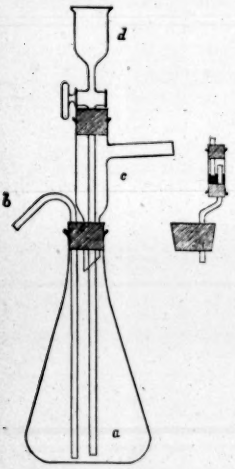
APPARATUS FOR KJELDAHL'S METHOD OF NITROGEN DETERMINATION.

BY H. P. ARMSBY AND F. G. SHORT.

One of the chief advantages of Kjeldahl's method for determining nitrogen is found in the fact that a number of determinations may be made simultaneously. So far as the oxidation is concerned, it is a comparatively simple matter to carry on any desired number

at once, since they require hardly any attention, but to carry on the subsequent distillation at an equally rapid pace with the common forms of apparatus requires a considerable expenditure of time.

We have therefore endeavored to devise a form of apparatus which should require as little attention as possible during its operation, and should allow us to conduct several distillations at the same time. The apparatus has proved so satisfactory in its operations that we are induced to describe it.



A flask *a*, of any desired form, and of a capacity of about a litre, is closed by a large rubber stopper which carries three tubes. Of these, *b* reaches as nearly as possible to the bottom of the flask, and serves to empty it after the distillation is completed. This is most conveniently done by connecting it with a Richards jet pump. The tube *c* is the exit tube. Where it passes through the stopper it has an interior diameter of about 12 mm., and widens above to about 25 mm. At one side, near the top, is attached an exit tube of such size as to be readily connected with a block-tin condenser. This tube inclines slightly upward. The tube *c* is open at the top, the opening being closed by a rubber stopper carrying a funnel tube *d*, whose stem extends nearly to the bottom of the flask *a*. The annular space about the stem of the funnel tube is filled with glass beads, to arrest any particles of alkali which may be carried over mechanically. The exit tube of *c* is connected with a block-tin condenser the copper jacket of which is 38 cm. long and 5 cm. in diameter and stands at an angle of about 20° with the vertical. To the lower end of the condenser is attached a glass tube dipping into the standard acid contained in a suitable vessel. In our apparatus six flasks and condensers are placed side by side. The con-

densers are firmly fastened to a light wooden frame, and the water enters at one side and passes through all the condensers successively. The flasks stand upon wire gauze stretched upon two horizontal iron rods about 12 cm. apart, and are sufficiently steadied above by the connection with the condenser. Under each flask is a Bunsen burner, connected by means of a gas-cock with the pipe which supplies the whole. The apparatus is placed upon a small table mounted on casters, and, by simply disconnecting the water and gas, can be wheeled to one side when not in use.

The operation of the apparatus is obvious from the figure. The flask *a* is filled through the funnel tube *d*, the ammonia is evolved through the tube *c*, *b* being closed by means of a pinch-cock, and at the close of the operation the flask is emptied through *b*, as already explained. Water is then poured in through *d* and evacuated through *b*, and the flask is ready for the next distillation.

In order to prevent regurgitation of the standard acid, the stopper of the flask *a* carries, in addition to the two tubes just described, a small mercury trap, as shown in the small figure at the right. The action of this is sufficiently obvious without description. With us it has never failed to prevent any dangerous regurgitation, even with very irregular distillation.

In order to test the apparatus, eleven determinations of nitrogen were made upon a sample of pure ammonium chloride, with the following results:

Nitrogen in Pure NH_4Cl.

1	25.85 per cent.
2	26.21
3	26.52
4	26.39
5	26.53
6	25.78
7	25.84
8	26.31
9	26.17
10	26.34
11	26.31
Average	26.21 $\pm$ 0.05 per cent.
Calculated	26.24 per cent.

The probable error of a single determination is $\pm$ 0.18 per cent.

of the substance analysed, or ± 0.69 per cent. of the total amount of nitrogen determined.

For the purpose of estimating the error involved in the combined processes of oxidation and distillation, eleven determinations of the nitrogen in a sample of wheat bran were made, with the following results:

Nitrogen in Wheat Bran.

1	2.54 per cent.
2	2.52
3	2.52
4	2.45
5	2.48
6	2.47
7	2.40
8	2.45
9	2.47
10	2.52
11	2.46
Average	2.48 ± 0.008 per cent.
" of 12 determinations by soda lime	2.43 ± 0.015

The probable error of a single determination is ± 0.028 per cent. of the substance analysed, or ± 1.13 per cent. of the total amount of nitrogen determined.

For the determinations of nitrogen in ammonium chloride about 0.12—0.14 gram was usually weighed out; for those in wheat bran 0.5 gram was uniformly taken. The ammonia was received in titrated hydrochloric acid and the excess of acid determined by titrated ammonia, with cochineal tincture as indicator. The fluids had been recently prepared, and the strength of the acid determined by means of pure sodium carbonate; 1 cc. of it was equivalent to .00497 gram of nitrogen. Acid and alkali were measured in calibrated burettes reading to $\frac{1}{20}$ cc. and permitting the estimation of $\frac{1}{100}$ cc.

In addition to the above test-analyses, the apparatus has been used for the regular work of the station for some months. Over 300 determinations have been made by its aid on samples of fodders, milk and fertilizers, and with uniformly satisfactory results, both as regards the apparatus and the method.

Communications from the Chemical Laboratory of Wesleyan University.

II.—ON THE LOSS OF NITROGEN BY PLANTS DURING GERMINATION AND GROWTH.

By W. O. Atwater and E. W. Rockwood.

The apparent escape of nitrogen in several experiments by one of us on the acquisition of atmospheric nitrogen by plants,[1] rendered a study of the question of the liberation of nitrogen from its compounds in germinating seeds desirable. A beginning was attempted in the following experiments.

The question proposed was this: In the germination of seeds and early growth of plants—in this case, peas—may there be any such loss of nitrogen as to materially affect the results of such experiments as those just referred to?

The plan of the experiments consisted in causing peas to germinate under appropriate conditions and cultivating the germinated plants for a longer or shorter time in water or sand. The nitrogen in the seed at the outset was estimated by determining the nitrogen in other peas of the same lot, assuming those experimented with to have the same percentage of nitrogen, weighing the peas used for seed, and computing the nitrogen in them. The nitrogen in the germinated seeds or young plants was determined directly. In the cases in which the plants grew in sand the quantity of nitrogen left behind in the sand at the end of the experiment was determined also. The nitrogen was determined by soda-lime and by Kjeldahl's method, the results by the two methods agreeing closely. The difference between the amounts of nitrogen at the beginning and the end of the experiment showed the loss during germination and growth.

The time of the experiments varied from six to fifty-two days, reckoning from the day when the seeds were first moistened and set to germinating to that when the growth was stopped and the plants taken for analysis. The plants as analysed were thus in various stages of development, from that in which germination was hardly completed to that in which the plants were well on in growth, if the latter expression may be applied to plants which had no food except that contained in the seed and acquired from the air.

[1] This Journal **6**, 365.

Three series of experiments were made. In those of the first series, which were intended as preliminary tests, the plants had their roots immersed in water. In the second and third series they grew in sand which was kept moistened with water. The water in each case was freed from nitrogen compounds by distilling in the ordinary way, and then redistilling with potassium hydroxide and permanganate, and rejecting so much of the second distillate as gave any visible reaction for ammonia with Nessler's reagent. The remainder of the distillate was regarded as free from nitrogen compounds, and was used for the experiments. The sand was freed from nitrogen compounds by washing and ignition. Portions tested with soda-lime gave no traces of ammonia.

First Series.—Water Culture, in Open Air.

This series included three experiments—Nos. 1, 2 and 3. The peas were germinated in moist paper, and then suspended with the radicles immersed in water as is commonly done in water culture. They were placed in the open window of a room adjoining the main room of our chemical laboratory. The plants were thus protected from rain and dew while exposed to the air. Though the doors connecting with the laboratory were kept closed, some ammonia compounds from the laboratory may very probably have found their way around, through the air outside, to the young plants. The error thus introduced would, of course, decrease the apparent loss of nitrogen. The very minute quantities of nitrogen left behind in the nutritive solutions in the experiments of the succeeding series make it extremely improbable that any considerable quantity of nitrogenous compounds in these experiments could have passed from the seeds or plants into the solutions. At the end of the experiment, when growth was stopped and the plants were taken for analyses, those of Experiment No. 1 were 2—6 cm.; those of No. 2, 3—5 cm.; and those of No. 3, 2—6 cm. in height. The results are stated herewith.

TABLE I.

Experiments in Water Culture, in Open Air.

Exp't No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.			
			In Seeds at beginning of Experiment.	In Plants at end of Experiment.	Lost during Germination and Growth.	
					Total.	Per Cent.[1]
		days.	mgm.	mgm.	mgm.	
1	23	8	215.6	197.5	18.1	8.4
2	8	10	67.5	60.9	6.6	9.8
3	5	15	41.4	40.8	0.6	1.5

The fact that the plants fifteen days after germination showed so little loss of nitrogen, only 1.5 per cent. of the total nitrogen of the seeds, may very likely have been due to absorption of ammonia from the air by the water and the foliage. The results of this and of the other experiments, as well as *a priori* considerations, would lead to the supposition that no definite and regular relation exists between the time of duration of the experiment and the amount of nitrogen lost. That the absorption of ammonia, which would be expected in an atmosphere containing ammonia salts, does actually take place to a large extent even so early in the period of growth, was shown by two experiments, Nos. 4 and 5, which were made in the same manner as Nos. 1, 2 and 3, except that the plants stood inside the window of one of the working rooms of the laboratory. At the time of the experiments the laboratory was used but little, and much less ammonia was afloat in the air than usual. The window was closed most of the time. At the end of the experiment the plants were from 1 to 6 cm. high. Nessler's reagent gave visible traces of ammonia in the water. The results are annexed.

TABLE II.

Plants in Air of Laboratory. Water Culture.

Exp't. No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.			
			In Seeds at beginning of Experiment.	In Plants at end of Experiment.	Gain.	
					Total.	Per Cent.
		days.	mgm.	mgm.	mgm.	
4	29	9	290.2	309.4	19.2	6.6
5	12	9	119.7	129.9	10.2	8.5

[1] Of amount in seeds at beginning.

It is possible that part of the loss of nitrogen observed in Nos. 1, 2 and 3 may have been due to solution of nitrogenous matter by the water in which the roots were immersed. Though this source of error, as already stated, was in all probability extremely small, an attempt to avoid it was made in experiments in sand culture, in which the nitrogen left in the water about the roots was also determined.

SECOND, THIRD AND FOURTH SERIES.—SAND CULTURE, IN OPEN AIR AND IN GREENHOUSE, ETC.

The peas of these series were either germinated in sand, in which they were allowed to remain a longer or shorter time for subsequent growth, or first germinated in a Nobbe's apparatus and then transferred to sand. The sand was contained in either small beakers or porcelain evaporating dishes, and kept reasonably moist during the experiment.

Second Series, Nos. 6, 7 and 8.—The peas, 12 in number, of each experiment were planted in sand in a small beaker. The sand was from 3 to 4 cm. deep, though the peas were covered to less depth. The beakers were kept in the open air, but protected from rain and dew. At the end of the experiment the beakers with their contents were heated in a drying oven to stop the growth. Within a day or two the sand was separated as accurately as convenient, both sand and plants were dried, and the nitrogen was determined in each. Results are given in Table III beyond. Here follow some of the details.

No. 6.—Time, 6 days. Radicles 1—4 cm. long. But one plumule had appeared above the sand, though the growth seemed to be normal.

No. 7.—Time, 10 days. Radicles 2—5 cm. long. One plumule in sight above the sand.

No. 8.—Time, 14 days. Radicles 2—5 cm. long. One plumule above the sand. One pea had not sprouted. A crust, which seemed to contain organic matter, had formed on the top of the sand. Decided indications of decay were apparent. The experiment appears, therefore, to have been abnormal.

Third Series, Nos. 9, 10 and 11.—The peas in each case were germinated in a germinating apparatus, and then transferred to a porcelain capsule, covered with sand and placed in a greenhouse.

No. 9.—Time, 4 days in germinating apparatus and 14 in sand; total, 18 days. Radicles 1—2 cm. long when taken from apparatus. Plants at end of experiment about 3 cm. high.

No. 10.—Time, 6 days in germinating apparatus and 22 in sand; total, 28 days. Radicles 1—2 cm. long when taken from apparatus. Vines 2—5 cm. high at end of experiment.

No. 11.—Time, as No. 10, except that the plants remained 46 days in the sand, making the whole period 52 days. The plants were from 13 to 15 cm. high, but had not seemed to grow much during the last two weeks, and the leaves had begun to turn yellow. Tendrils had appeared.

Fourth Series, Nos. 12 and 13.—Method as in previous series, but experiments made some weeks later and in a dwelling-house.

No. 12.—Total time, 29 days. Vines 2—7 cm. high. The peas with the smallest vines showed signs of decay.

No. 13.—Time, 42 days. Vines 6—10 cm. high, had not grown for some time. Leaves had begun to turn yellow, as was the case in No. 11.

In both 12 and 13 the sand was washed from the roots with water, and the washings dried with the sand for nitrogen determination. Oxalic acid was added to the washings to prevent loss of ammonia.

In several of the above cases portions of the sand were treated with water, and the extract concentrated and tested for nitrates with ferrous sulphate and sulphuric acid. In No. 8, in which one of the peas failed to sprout, there was a faint trace; in the others none were found. Besides the plainly visible marks of decay in No. 8, there were less decided indications of decay in some of the others.

In the experiments in sand culture very minute quantities of nitrogen were left in the sand. Part of this, in the second and third series at least, came from the minute fragments of the roots, which were not easily separated from the sand. The inference is, that only extremely small quantities of soluble nitrogenous compounds could have been extracted from the roots by the water which surrounded them. It seems fair to infer, as above stated, that but little of the loss observed in the first series could have been due to this cause.

TABLE III.

Experiments in Sand Culture.—Second Series, in Open Air; Third, in Greenhouse; Fourth, in a Room of a Dwelling-House.

Series.	Exp't No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.					
				At beginning of Exp't. In Seed.	At end of Experiment.			Loss during Germination and Growth.	
					In Plants.	In Sand.	Total.		
			days.	mgm.	mgm.	mgm.	mgm.	mgm.	per cent.
2d	6	12	6	100.3	91.7	2.6	94.3	6.0	5.9
	7	12	10	102.9	89.2	2.8	92.0	10.9	10.6
	8	12	14	109.7	81.5	11.6[1]	93.1	16.6	15.1
3d	9	12	18	115.6	100.3	6.9[1]	107.2	8.4	7.3
	10	12	28	103.4	83.2	7.5[1]	90.7	12.7	12.4
	11	12	52	101.4	80.9	4.0[1]	84.9	16.5	16.3
4th	12	10	29	88.3	81.1	...	81.1	7.2	8.2
	13	10	42	88.2	75.6	2.9	78.5	9.7	11.0

It seems, then, that in each of these experiments nitrogen was liberated; that the loss in each series commenced during germination; that there was an apparent recovery in the experiments in water culture, due most probably to acquisition of nitrogen from the air in the form of ammonia or otherwise, but that in the experiments of the last three series the escape of nitrogen continued until the end. The probable causes of this loss demand at least a brief consideration.

THE LIBERATION OF NITROGEN IN GERMINATION AND GROWTH, BY DECAY AND OTHERWISE.

It has been urged—*e. g.*, by Duclaux[2] and Jorisson[3]—that the formation of diastase in germination depends upon the action of microbes. The loss of nitrogen from germinating seeds, and the fact that forms of fermentation which are clearly due to microbes are likewise accompanied by escape of nitrogen from its compounds, would, at first thought, seem to favor the belief that microbes are essential to germination. But the lately published observations of Laurent[4] imply that normal germination takes place independently of micro-organisms. The latter observer finds that the reduction of nitrates to nitrites in presence of germinating seeds, which others

[1] The sand contained considerable quantities of fragments of roots, etc.
[2] Compt. Rend. **100**, 67; See also observations of Pasteur, *loc. cit.* 68.
[3] Ber. **18**, II, 79. [4] *Ibid.* **19**, II, 33.

have attributed to microbes, is likewise caused by the seed itself in germinating in absence of microbes.

The decomposition of nitrogenous organic compounds and of nitrates in the presence of organic matter, with escape of nitrogen in the free state or in its lower oxides, is a fact well established, but not yet completely understood.[1]

Schlösing has shown[2] that nitrates may be decomposed in soil with evolution of free nitrogen. This appeared in Schlösing's experiments to be dependent upon the oxidation of organic matter at the cost of the oxygen of the nitrates.

Still later observations by Gayon and Dupetit,[3] and by Dehérain and Maquenne,[4] confirm the very large reduction of nitrates in presence of decomposing organic matter, and indicate that this denitrification is due to ferments, as has also been pointed out by Springer.[5] It appears that the presence of organic matter and the absence of oxygen are requisite to the action of these denitrifying ferments, and that not only free nitrogen, but its lower oxides and ammonia, are evolved.

At the beginning of his well-known studies upon the sources of the nitrogen of plants,[6] Boussingault tested the loss of nitrogen in the germination of clover and wheat. Seeds of clover germinated in air on a porcelain plate showed no considerable gain or loss of nitrogen up to the time when the leaves began to appear. Similar results were obtained with wheat, in which the experiment was continued until the green parts predominated in the seed and the stems were 3—5 centimeters long. Boussingault concluded that "clover and wheat in germinating neither gained nor lost nitrogen."

In experiments preliminary to their likewise well-known researches "On the Sources of the Nitrogen of Vegetation,"[7] Messrs. Lawes, Gilbert and Pugh made several series of experiments on the question of the escape of nitrogen from nitrogenous organic matter. In one series, wheat, barley and bean meal were mixed with ignited pumice and with ignited soil, put in a bottle through which washed air was passed, moistened, and kept from June 10 to October 8. In one case there was no loss of nitrogen, in five

[1] See Reiset, Compt. Rend. **42**, 53; Ville, *loc. cit.* **43**, 143; König and Kiesow, Landw. Jahrb. 1873, 107; Armsby, Am. Jour. Sci. [3], **8**, 337; Dietzell, Centbt. f. Ag. Chem. 1882, 417; Reder, *loc. cit.* 1884, 652; Morgen, Landw. Vs. St. **30**, 199 and 429; Kellner, *loc. cit.* **32**, 57; and others quoted beyond.

[2] Compt. Rend. **77**, 202 and 353. [3] Compt. Rend. **95**, 944. [4] *Loc. cit.* **95**, 691, 634.

[5] This Journal **4**, 452; Proc. Am. Asso. **18**, 172.

[6] Ann. Chim. Phys. [2], **67**, 5. [7] Phil. Trans. 1861, II, 499.

others from 3 to 13 per cent. of the nitrogen escaped, apparently as free nitrogen. In another series, seeds of wheat, barley and beans were kept under similar conditions from March 16 until August 18. The seeds germinated and the plants grew for a time, but finally decomposed. From none to 40 per cent. of the nitrogen escaped, one-eighth to one-half of the liberated nitrogen passing off in the form of ammonia. The authors were unable to trace any connection between the different conditions of the experiments and the quantities of nitrogen given off.

To learn to what extent nitrogen would be liberated from seeds or plants in more nearly normal conditions of growth, the same experimenters conducted a series of trials in which wheat, barley and beans were put in ignited pumice and ignited soil in pots and kept in confined air under a large glass shade 16 inches in diameter, on a table, in the diffused light of the laboratory. The plants were at first supplied with distilled water, but with no carbonic acid beyond that which might be contained in the water. The seeds were put in May 1st; the plants grew "tall, slender, delicate," until June 10th, when growth had ceased. Analysis showed no considerable difference between the quantities of nitrogen in the plants and in the seed. The authors conclude that their experiments "in regard to the question of assimilation will not be affected by a loss of free nitrogen, as the result of decomposition of nitrogenous organic matter, as long as that matter is subjected to the ordinary process of germination and exhaustion to supply materials for growth."

The specific question of the loss of nitrogen during the germination and subsequent growth of plants has been studied by several other investigators. Hellriegel caused seeds of winter rape (*Brassica nap. oleif.*) to germinate in confined air under glass. At the end of the period of germination, which, as it would appear from his description, he regarded as terminating when the cotyledons had turned green, no escape of nitrogen was detected by analysis.[1]

Schulz, in an extended series of trials,[2] in which seeds of Leguminosae and Cruciferae, lupine beans, pepper grass, etc., were germinated in presence of pure water in closed vessels, and the resulting gaseous mixtures analysed, found considerable quantities of nitrogen to be set free. He concludes that in the first *stadium* of germination, by which he designates the period which precedes the

[1] Jour. prac. Chem. **64**, 1855, 100 and 107. [2] *Loc. cit.* **87**, 1862, 129.

bursting of the seed-coat and the appearance of the radicle, there is, along with the purely endosmotic absorption of water and oxygen, a decomposition of albuminoid compounds with formation of carbonic acid and liberation of nitrogen, while hydrogen is set free later.

In the second *stadium*, by which he understands the time from the first visible formation of new cells to the formation of the first leaves, nitrogen, hydrogen and carbonic acid are evolved. The quantities of nitrogen liberated in his experiments were, in some cases, very considerable. Schulz very pertinently calls attention to the difference between the normal changes of germination and those of decay (*Fäulniss*), or *putréfaction*, as it was designated by Saussure, who, like Rolle, Ingenhousz, Sennebier and Davy, had previously studied the same subject. In experiments with seeds which had been crushed so as to prevent germination, and thereafter subjected to the same conditions as the seeds which germinated, nitrogen and carbonic acid were found in each case, but hydrogen in no case, in the gaseous mixture given off. That is to say, in the case of the germinating seeds, the liberation of nitrogen and hydrogen and carbonic acid accompanied germination, while in the putrefaction of the crushed seeds which could not germinate, carbonic acid and nitrogen were liberated without hydrogen. Schulz also very aptly insists on the differences between plants of different species in respect to the chemical changes in germination.

Day[1] has made experiments on the germination of barley, a collateral object being to ascertain whether atmospheric nitrogen takes any active part in the germination. The seeds were kept in confined air over mercury. He cites Mülder as saying that in germination a small quantity of nitrogen gas is absorbed, but finds in his own experiments that the total quantity of nitrogen in the confined volume of air in which the germinating barley was placed was sometimes increased and sometimes diminished to a very small extent, and infers that nitrogen takes no active part in the germination. He does not consider the liberation of nitrogen at all, but his results evidently show that no great quantity was lost.

In the experiments referred to at the beginning of this article as made by growing peas in sand with nutritive solutions, and which led to our experiments here detailed, the seeds germinated and the plants grew in the presence of the nitrates of the nutritive

[1] Jour. Chem. Soc. 1880, Trans. 646.

solutions. Boussingault[1] has reported a loss of nitrogen when seeds were germinated in presence of nitrates, which loss he refers to the nitrates rather than to the seeds. Ten beans, weighing 10.533 grams, were allowed to germinate in a barren soil to which 0.3 gram of potassium nitrate was added, the germination taking place in the dark. At the end of 21 days, nearly half (45.3 per cent.) of the nitrogen of the nitrate had disappeared, while neither plants nor soil contained any nitrogen compound into which the nitrogen lost from the nitrate could have been changed. The natural inference was that the nitrogen must have escaped in the form of gas. In an experiment with maize a still greater loss of nitrogen was observed. The development of the plants was, in Boussingault's opinion, too vigorous to admit the supposition that *débris* from the plants could have furnished organic matter to reduce the nitrates, and he was led to the supposition, afterwards strengthened by experiments made at his instigation, that the nitrates were reduced by organic matter excreted by the roots of the plants. This explanation was, however, suggested before the observations of Gayon and Dupetit, and others above mentioned, which indicate that the reduction of nitrates in presence of organic matter may be brought about by micro-organisms.

In his studies on nitrification by bacteria,[2] Warington calls attention to the "curious fact that when fresh soil [containing the nitrifying ferments] is added to .... solutions suitable for nitrification, a destruction of nitrates already present precedes the commencement of nitrification." This disappearance of the nitrates he refers to the reducing bacterium observed by Dehérain and Maquenne and others, and which are active in absence of oxygen.

Frankland and Jordan have studied the action of "hay bacilli," "the micro-organisms which convert grass into hay or ensilage," and which "exist in vast numbers in grass. In the presence of free oxygen they absorb this gas and evolve carbonic anhydride and nitrogen, and these are the gaseous products in the making of hay..... The absorption of oxygen is not necessary, for carbonic anhydride is evolved in an atmosphere of hydrogen; but under these circumstances very little nitrogen makes its appearance. The fermentation goes on under water, but its character is changed. The gases, which are much augmented in volume, now consist of

[1] Ann. Chim. Phys. [5], **22**, 1881, 433. [2] Jour. Chem. Soc. 1884, Trans. 669.

carbonic anhydride (84.63 per cent.), hydrogen (6.9 per cent.), nitrogen (5.83 per cent.), and traces of other combustible gases. Acetic acid, lactic acid, and probably butyric acid, are at the same time formed. This is probably the kind of fermentation by which grass is converted into ensilage."[1] Kellner and others have observed large losses of nitrogen from vegetable matters confined out of access of air, as is done in ensilage. Kellner, however, is not inclined to ascribe the loss of nitrogen to fermentation.[2]

Conclusions.—Loss of Nitrogen.

The results of the experiments above detailed, and the inferences which, in view of the facts at hand, seem to us warranted, may be thus summarised.

The conditions of the experiments and quantities of nitrogen lost were as in Table IV.

Table IV.

Conditions of Germination and Growth of Peas.	Experiments. Series.	No.	Time of Germination and Growth.	Nitrogen Lost, in Per Cent. of Total in Seed at beginning of Experiment.
Water Culture.				
Seeds germinated and then suspended with roots immersed in pure water. Experiments in open air.	1st.	3	8 days.	8.4 per cent.
		1	10 "	9.8 "
		2	15 "	1.5 "
Sand Culture.				
Seeds germinated and grown in sand. Experiments in open air.	2d.	6	6 days.	5.9 per cent.
		7	10 "	10.6 "
		8	14 "	15.1 "
Seeds germinated and then transferred to sand. Experiments in greenhouse.	3d.	9	18 days.	7.3 per cent.
		10	28 "	12.4 "
		11	52 "	16.3 "
Seeds germinated and then transferred to sand. Experiments in dwelling-house.	4th.	12	29 days.	8.2 per cent.
		13	42 "	11.0 "

In the experiments of the first series, in which the peas were germinated in paper and thereafter kept a short time in open air, with the roots in water, there was in each case a loss of nitrogen. The loss was largest, 9.8 per cent., in the case where growth was stopped at the end of ten days. The failure to find any consider-

[1] Jour. Chem. Soc. 1885, Trans. 180.

[2] Landw. Vs. St. **32**, 56, 71.

able amount of nitrogen in the water about the seeds in the sand experiments implied that very little nitrogen could have been taken from the seeds by the water. Where the plants were allowed to grow five days longer the loss was only 1.5 per cent. This last result may be explained by acquisition of nitrogen as ammonia or otherwise from the air, the loss being thus nearly made up. It will be remembered that the plants of this series were grown near the chemical laboratory, from which ammonia compounds would naturally escape into the air and thus become available to the plants.

In the experiments of the second series, in which the seeds were germinated and grown in sand and kept in open air long enough to make the whole duration of the experiment from 6 to 14 days, the loss of nitrogen varied from 5.9 per cent. in 6, to 15.1 per cent. in 14 days. There was, therefore, either larger loss of nitrogen or less acquisition of nitrogen in the longest period than in the experiment in water culture.

In the experiments of the third and fourth series, in which the seeds were germinated in a germinating apparatus during 4—6 days, and were then put in sand and grown in a greenhouse (3d series) or in a dwelling-house (4th series) for longer periods, there was in each case a loss of nitrogen. The loss in each series increased with the duration of the experiment.

In the first two experiments of each of the first two series, the plants had passed but little beyond the period of germination proper. The loss of nitrogen in each of these four cases was from about 5 to 10 per cent. of the whole nitrogen in the seed.

The increased loss of nitrogen with increased duration of the experiments in the last three series indicates that the liberation of nitrogen, which commenced when the seeds were germinating, continued during the whole life of the plants.

In two cases, Nos. 8 and 12, there were very evident indications of decay. That there may have been decay in the other cases seems to us not improbable. The supposition, indeed, seems most reasonable, when we consider how often decay is observed in seeds during and after the period of germination.

The data from other sources above cited show that decomposition of nitrogenous matters, organic and inorganic, is often, but not always, accompanied by liberation of nitrogen; that the decomposition is often, if not always, dependent upon microbes; and that, in

many cases at least, the liberation of nitrogen is due to microbes. It is therefore difficult to avoid the inference, although the proof is not absolute, that all three phenomena—action of microbes, decomposition, and liberation of nitrogen—are correlated.

As regards germination, the best evidence at hand seems to us to imply that the agency of microbes is not essential to the normal process. The facts that nitrogen is sometimes, but not always, liberated from germinating seeds, and that the liberation was observed, in our experiments particularly, to continue long after the period of germination had passed, coupled with the well-attested presence of microbes in many cases in which loss of nitrogen has been observed, and their undeniable action in liberating nitrogen, would seem to indicate that both their presence and the liberation of nitrogen are incidental concomitants of germination, and by no means essential to the process. They might thus be regarded as forms of decay, which, like other forms of disease, in higher as well as in lower organisms, either do not appear or are strongly pronounced, according to the circumstances of each case.

The general conclusions which these considerations seem to us to warrant may be still more briefly summarised as follows:

1. The decomposition of nitrogenous organic matter, living and dead, and of nitrates as well, is often attended by evolution of nitrogen in either the free state or in its compounds, or in both. This liberation of nitrogen is sometimes, if not always, due to microbes. It may be large or inappreciable, according to the circumstances of each case.

2. The germination of seeds is sometimes, but not always, accompanied by loss of considerable quantities of nitrogen. The balance of evidence at hand seems to us to decidedly favor the hypothesis that germination without microbes and without the liberation of nitrogen is the normal process.

3. In this view both the action of microbes and the liberation of nitrogen, either in the free state or in the lower oxides or ammonia, which has been attested not only in germinating seeds, but in the later periods of growth of the plant, must be regarded as simply forms of decay. They would thus be not essential to germination and growth, but accessory phenomena like the zymotic diseases that attack higher organisms.

The bearing of these considerations upon experiments on the acquisition of nitrogen by plants will be discussed in a succeeding article.

Analytical Details.

Nitrogen in Peas.

	Wt. of Peas. grams.	N Found. gram.	Per Cent. of N.	
Peas used in Series I, Nos. 1 and 2.	1.0242	.03699	3.61	3.59 per ct. of N in peas before germination.
	.8789	.03131	3.56	
	Two determinations gave	by another analyst	3.62 3.57	

	Wt. of Peas. grams.	N Found. gram.	Per Cent. of N.	
Peas used in Series I, No. 3, and subsequent experiments.	1.000	.03808	3.81	Average, 3.77 per ct.
	1.000	.03699	3.70	
	1.000	.03790	3.79	

Water-free Substance of Peas, and Nitrogen in Same.

	Wt. of Peas. grams.	Wt. of Water-free Substance. grams.	Per Cent. of Water-free Substance.	
Used in Series I, No. 3.	.9361	.8391	89.64	Average, 89.68 per cent.
	1.1523	1.0339	89.72	
	3.77 per cent. + 89.68 per cent. = 4.20 per cent. N in water-free substance.			
Used in Series II and III.	.8229	.7287	88.55	Average, 88.48 per cent.
	1.0756	.9508	88.40	
	3.77 per cent. + 88.48 per cent. = 4.26 per cent. N in water-free substance.			
Used in Series IV.	.5364	.4891	91.18	Average, 91.14 per cent.
	.5193	.4731	91.10	
	3.77 per cent. + 91.14 per cent. = 4.14 per cent. N in water-free substance.			

Nitrogen in Plants and Sand After Growth.

First Series.

	Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
No. 1.	.3702	.01552	4.19	Average, 4.19 per cent.
	.5500	.02301	4.18	
	1.8810 grams peas before germination		@ 3.59 per ct. = .0675 gram N.	
	1.4540 grams plants after growth		@ 4.19 per ct. = .0609 "	
			Loss = .0066 "	
			= 9.8 per cent.	
No. 2.	.2069	.01002	4.84	Average, 4.84 per cent.
	.2259	.01092	4.84	
	1.1540 grams peas before germination		@ 3.59 per ct. = .0414 gram N.	
	.8428 gram plants after growth		@ 4.84 per ct. = .0408 "	
			Loss = .0006 "	
			= 1.5 per cent.	

No. 3.

.5000	.02039	4.08	Average, 4.09
.5000	.02049	4.10	per cent.

5.7180 grams peas before germination =
5.1279 grams w.-fr. @ 4.20 per cent. = .2156 gram N.
4.8295 grams plants after growth @ 4.09 " = .1975 "
Loss = .0181 = 8.4 pr. ct.

No. 4.

.5000	.02544	5.09	Average, 5.09
.5000	.02544	5.09	per cent.

6.0780 grams plants after growth @ 5.09 per cent. =
.3094 gram N in plants.
7.6982 grams peas before germination =
6.9037 grams w.-fr. @ 4.20 per cent. = .2902 gram N.
.3094 gram — .2902 gram = .0192 gram N gained = 6.6 per cent.

No. 5.

.5000	.02419	4.84	Average, 4.80
.5000	.02374	4.75	per cent.

2.7083 grams plants after growth @ 4.80 per cent. =
.1299 gram N in plants.
3.1791 grams peas before germination =
2.8510 grams w.-fr. @ 4.20 per cent. = .1197 gram N.
.1299 gram — .1197 gram = .0102 gram N gained = 8.5 per cent.

Second Series.

No. 6.

Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
.5871	.02199	3.74	Average, 3.73
.5398	.02010	3.72	per cent.

2.4573 grams plants after growth @ 3.73 per cent. =
.0917 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
7.2961	.00100	.013	Average, .012
6.6435	.00070	.011	per cent.

21.1088 grams sand @ .012 per cent. = .0026 gram N in sand.
2.6620 grams peas before germination =
2.3553 grams w.-fr. @ 4.26 per cent. = .1003 gram N.
.1003 gram — (.0917 gram + .0026 gram) =
.0060 gram N lost = 5.9 per cent.

No. 7.

Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
.5182	.01701	3.28	Average, 3.24
.4592	.01463	3.19	per cent.

2.7523 grams plants after growth @ 3.24 per cent. =
.0892 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
6.1931	.00090	.014	Average, .015
6.7515	.00109	.016	per cent.

18.5573 grams sand @ .015 per cent. = .0028 gram N in sand.
2.7301 grams peas before germination =
2.4156 grams w.-fr. @ 4.26 per cent. = .1029 gram N.
.1029 gram — (.0892 gram + .0028 gram) =
.0109 gram N lost = 10.6 per cent.

	Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
	.5087	.01851	3.64	Average, 3.62
	.5240	.01881	3.59	per cent.

2.2518 grams plants after growth @ 3.62 per cent. =
.0815 gram N in plants.

	Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
No. 8.	6.8208	.00418	.061	Average, .060
	5.8250	.00348	.059	per cent.

19.3000 grams sand @ .06 per cent. = .0116 gram N in sand.
2.9103 grams peas before germination =
2.5750 grams w.-fr. @ 4.26 per cent. = .1097 gram N.
.1097 gram — (.0815 gram + .0116 gram) =
.0166 gram N lost = 15.1 per cent.

THIRD SERIES.

	Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
	.5000	.01620	3.24	Average, 3.28
	1.0000	.03329	3.33	per cent.

3.0585 grams plants after growth @ 3.28 per cent. =
.1003 gram N in plants.

	Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
No. 9.	6.0115	.00216	.036	Average, .028
	6.0000	.00118	.020	per cent.

24.7210 grams sand @ .028 per cent. = .0069 gram N in sand.
3.0663 grams peas before germination =
2.7130 grams w.-fr. @ 4.26 per cent. = .1156 gram N.
.1156 gram — (.1003 gram + .0069 gram) =
.0084 gram N lost = 7.3 per cent.

	Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
	1.0000	.0198	1.98	Average, 2.00
	.5000	.0101	2.02	per cent.

4.1576 grams plants after growth @ 2.00 per cent. =
.0832 gram N in plants.

	Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
No. 10.	8.0000	.00147	.018	Average, .022
	8.0000	.00206	.026	per cent.

34.1620 grams sand @ .022 per cent. = .0075 gram N in sand.
2.7430 grams peas before germination =
2.4270 grams w.-fr. @ 4.26 per cent. = .1034 gram N.
.1034 gram — (.0832 gram + .0075 gram) =
.0127 gram N lost = 12 4 per cent.

	Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
	1.000	.01584	1.58	Average, 1.55
No. 11.	1.000	.01525	1.52	per cent.

5.2190 grams plants after growth @ 1.55 per cent. =
.0809 gram N in plants.

No. 11.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
8.000	.00099	.012	Average, .011
8.000	.00069	.009	per cent.

35.998 grams sand @ .011 per cent. = .004 gram N in sand.
2.6914 grams peas before germination =
2.3813 grams w.-fr. @ 4.26 per cent. = .1014 gram N.
.1014 gram — (.0809 gram + .0040 gram) =
.0165 gram N lost = 16.3 per cent.

FOURTH SERIES.

No. 12.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.7675	.0196	1.11	Average, 1.11
1.7676	.0195	1.10	per cent.

7.3042 grams plants after growth @ 1.11 per cent. =
.0811 gram N in plants.
The sand contained no nitrogen.
2.3407 grams peas before germination =
2.1333 grams w.-fr. @ 4.14 per cent. = .0883 gram N.
.0883 gram — .0811 gram = .0072 gram N lost = 8.2 per cent.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.4095	.0199	1.41	Average, 1.37
1.4095	.0186	1.32	per cent.

5.5147 grams plants after growth @ 1.37 per cent. =
.0756 gram N in plants.

No. 13.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
11.9095	.0007	.006	Average, .005
11.9095	.0005	.004	per cent.

50.8123 grams sand @ .005 per cent. = .0029 gram N in sand.
2.3378 grams peas before germination =
2.1306 grams w.-fr. @ 4.14 per cent. = .0882 gram N.
.0882 gram — (.0756 gram + .0029 gram) =
.0097 gram N lost = 11.0 per cent.

Contributions from the Sheffield Laboratory of Yale College.

XXIII.—ON NEW ACID PROPIONATES AND BUTYRATES.

BY W. G. MIXTER.

Acid Barium Propionate, $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$.—Some time ago Mr. F. M. Strong, of this laboratory, attempted to make barium propionate by adding an excess of freshly prepared

barium carbonate to dilute propionic acid. The filtered solution was concentrated until crystals of normal barium propionate separated. The mother-liquor, on standing, yielded tabular crystals unlike those of the normal salt, and which were found to have composition given in Analysis I.

Analysis II is of crystals which formed from a solution of barium propionate containing a large excess of propionic acid, which stood some months in a desiccator containing sulphuric acid. Both lots of crystals were dried between blotting paper. The following are Mr. Strong's analyses:

	Calculated for $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$.	I.	II.	
Ba	33.33	32.42	33.42	33.49
C_9	26.27	27.00	25.68	...
H_{22}	5.35	5.86	5.50	...
O_9	35.05	...	...	...
	100.00			

A portion of substance used for Analysis II was heated to 100°, and after five days ceased to lose weight. The loss was 30.97 per cent.; theory requires 31.14 per cent. of $C_3H_6O_2 + 3H_2O$ in $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$. The acid salt gives off water and acid in dry air at ordinary temperatures, and after some months the anhydrous normal salt is left. The acid barium propionate partly liquefies at 64°, and at 100° some solid salt remains in the liquid. It should be stated that mixtures of the normal and acid salt were obtained in some attempts to make the acid salt.

Acid Strontium Propionate, $(C_3H_5O_2)Sr.C_3H_6O + 3\frac{1}{2}H_2O$.—The writer has recently prepared an acid strontium salt by dissolving strontium oxide in dilute propionic acid, adding as much more acid, and boiling down the solution until crystals separated on cooling. The evaporation was continued some days at ordinary temperature. The long, thin crystals were dried between blotting paper and analysed, with the following results:

	Calculated for $(C_3H_5O_2)_2Sr.C_3H_6O_2 + 3\frac{1}{2}H_2O$.	I.	II.
Sr	23.62	23.66	23.55
C_9	29.14	28.59	28.36
H_{23}	6.21	6.48	6.10
$O_{9\frac{1}{2}}$	41.03	...	...
	100.00		

Another preparation of the salt was heated for 24 hours to 100°, when it ceased to lose weight. The loss was 36.45 per cent.; theory requires 36.16 per cent. for a loss of $C_3H_6O_2 + 3\frac{1}{2}H_2O$, and 37.02 per cent. for $C_3H_6O_2 + 4H_2O$. The acid strontium propionate gives off propionic acid on exposure to the air, and after a few hours is coated with a white powder. It partly melts at 67°, and completely liquefies at 75°.

Acid Calcium Propionate, $2[(C_3H_5O_2)_2Ca].C_3H_6O_2 + 5H_2O$. —Acid calcium propionate was obtained in long needles by the evaporation over sulphuric acid of a solution which was prepared by adding a liberal quantity of dilute propionic acid to a saturated solution of calcium propionate. The crystals were dried with filter paper. Analysis I is of the first crop of crystals, and Analysis II is of crystals from the mother-liquor of the first lot.

	Calculated for $2[(C_3H_5O_2)_2Ca].C_3H_6O_2 + 5H_2O$.	I.	II.
C_{15}	33.58	33.34	33.31
H_{36}	6.72	6.72	6.74
Ca_2	14.92	15.03	15.01
O_{15}	44.78	...	...
	100.00		

The salt reacts acid and gives off acid on exposure to air. It does not melt on heating, but softens and chars. At 100° 0.7215 gram lost, in 8 hours, 0.1594 gram, and in 24 hours, 0.1674 gram, and a solution of the residue was acid to litmus paper. Attempts were made to prepare an acid salt by boiling an acid solution of calcium propionate until crystals separated, and also by allowing an acid solution to evaporate in the open air. Neither lot of crystals was acid to test paper, and both contained calcium corresponding to $(C_3H_5O_2)_2Ca + 2H_2O$.

Acid Barium Isobutyrate, $(C_4H_7O_2)_2Ba.C_4H_8O_2$.—Mr. H. E. Andrews, of this laboratory, made acid barium propionate at the time Mr. Strong did, and then undertook the preparation of an acid butyrate. He dissolved 20 grams of barium isobutyrate in a small bulk of water, and added a liberal excess of isobutyric acid. The viscous solution was evaporated on a water bath until it solidified on cooling. The salt was then heated to 100° until its weight was constant. The following is Mr. Andrews' analysis:

	Calculated for $(C_4H_7O_2)_2Ba.C_4H_8O_2$.	Found.
Ba	34.33	34.00
C_{12}	36.08	36.19
H_{22}	5.51	5.80
O_6	24.08	...
	100.00	

Acid barium isobutyrate becomes viscid at 74°.

The barium and strontium salts described are analogous, except in water content, to the acid acetates $(C_2H_3O_2)_2Ba.C_2H_4O_2 + 2H_2O$ and $(C_2H_3O_2)_2Sr.C_2H_4O_2 + 2H_2O$.[1] The propionic acid used in the experiments was made from propionitrile.

XXIV.—ON PARA-FORM-NITR-ANILIDE.

By T. B. Osborn and W. G. Mixter.

Para-form-nitr-anilide was made for the purpose of obtaining, by the action of zinc and ammonia upon it, form-azo and form-azoxy bodies. We failed to get any pure compounds. Reduction with ammonium sulphide also gave negative results. Huebner[2] prepared *o*-form-nitr-anilide melting at 122° from *o*-nitraniline and formic acid. *p*-Form-nitr-anilide does not appear to have been described. We made it by adding formanilide slowly to red, fuming nitric acid, specific gravity 1.53, cooled by a mixture of snow and salt. The temperature of the acid was kept below 10°. The acid solution was poured into cold water, and the precipitated form-nitr-anilide was washed with ice-water, and finally with ether. It was crystallised from absolute alcohol and was analysed, with the following results:

	Calculated for $C_6H_4NO_2NHCOH$.	I.	II.
Carbon,	50.60	49.98	50.04
Hydrogen,	3.62	3.61	3.81
Nitrogen,	16.86	17.18	17.11
Oxygen,	28.92	...	...
	100.00		

[1] Villiers, Bulletin de la Société chimique **30**, 176. [2] Ann. Chem. **209**, 339.

p-Form-nitr-anilide is sparingly soluble in hot water, and separates, on cooling, in brownish-red crystals which melt at 192° to 194°. The crystals from absolute alcohol melted at 187°. When distilled with very dilute sulphuric acid the distillate gave reactions for formic acid. Boiled with potassium hydroxide and cooled, yellow, needle-shaped crystals separated, soluble in hydrochloric acid and melting at 143°, showing that *p*-nitraniline was formed.

XXV.—ON PARA-DIBROM-ORTHO-AZO-ACETANILIDE

By C. H. Matthiessen and W. G. Mixter.

Some time ago one of us (W. G. M.) failed to obtain an azo-body by reducing an ammoniacal solution of *o*-nitracetanilide with zinc. A preliminary experiment with brom-*o*-nitranilide indicated the easy preparation of a new compound. We found, however, great difficulty in obtaining pure products. The material used was made by carefully nitrating *p*-bromanilide, melting-point 165°, and crystallising the product from alcohol. It had the melting-point of *p*-brom-*o*-nitracetanilide, and was found to contain nearly the required amount of bromine and nitrogen. In the first experiment brom-nitranilide, 20 grams, was dissolved in hot alcohol, and concentrated ammonia water and platinised zinc powder were added. The brownish-red precipitate which formed remained several days in contact with the zinc. It was filtered, washed with alcohol, digested with dilute hydrochloric acid, and then thoroughly washed with water and alcohol. The yield was 3.9 grams. An analysis showed the absence of oxygen in the substance, and gave results corresponding fairly well with the empirical formula $C_{12}H_{12}Br_2N_4$. This result indicates that the substance is impure brom-azo-aniline; but the fact that it is insoluble in alcohol and hydrochloric acid does not sustain this view. The small quantity of material prevented further investigation of this product of the long action of zinc on brom-nitranilide.

In another experiment 40 grams of brom-nitranilide were dissolved in not sufficient hot alcohol to hold all in solution when cold. To the hot solution strong ammonia water and a large quantity of platinised zinc were added. The whole was frequently shaken. The action was rapid, and was allowed to continue only half an

hour. The precipitate was treated as described in the first experiment. Its weight after drying at 100° was 10 grams. The filtrate did not yield another precipitate on further treatment with zinc, and on evaporation left a sticky residue. The following is the analysis of the dry precipitate:

	Calculated for $C_6H_3BrNNHC_2H_2O$. ‖ $C_6H_3BrNNHC_6H_2O$.	Found.		
C_{16}	42.29	43.07	...	...
H_{14}	3.09	3.19	...	...
Br_2	35.24	31.21	31.23	31.03
N_4	12.33	12.79	12.56	...
O_2	7.05	...	...	...
	100.00			

The deficiency in bromine is possibly due to the removal of this element by nascent hydrogen with formation of some azo-acetanilide. On the supposition that this latter body was present, attempts were made to separate it by means of hot hydrochloric acid, experience having shown that *p*-azo-acetanilide is readily saponified by the acid.[1] In the first trial a portion of the substance was placed in a large bulk of concentrated hydrochloric acid, and the whole was evaporated nearly to dryness on a water bath. The residue, after washing and drying, was found to contain 32.53 per cent. of bromine. Another portion of the substance was placed in a sealed tube with concentrated hydrochloric acid and heated for four hours to 100°. The larger part of the compound remained unaltered. After washing carefully and drying at 100°, it was analysed, with the following results:

	Calculated for dibromazoacetanilide.	Found.	
C_{16}	42.29	42.23	...
H_{14}	3.09	3.04	...
Br_2	35.24	34.22	...
N_4	12.33	13.13	13.14
O_2	7.05	...	...

p-Dibrom-*o*-azoacetanilide has a light red color, is insoluble in alcohol, chloroform and glacial acetic acid. It melts at 280–282°. It is saponified with difficulty by a boiling solution of potassium

[1] Mixter, this Journal **5**, 284.

hydroxide in alcohol, yielding a dark red, feebly basic body, which is soluble in alcohol. We tried several times to make dibromazo-anilide by saponifying the dibrom-azo-acetanilide, and failed to obtain a pure product, or even one free from oxygen.

XXVI.—ON HALOGEN DERIVATIVES OF OXANILIDE.

By J. O. Dyer and W. G. Mixter.

The action of the halogens on oxanilide has been studied but little. Gerhardt,[1] by treating oxanilide with bromine, obtained a substance soluble in ether, which is not further described, except that it crystallises from the ethereal solution. Wallach,[2] by acting upon oxanilide with phosphorus pentachloride, and treating the product with hydrogen sulphide, got thio-oxanilide. This compound was doubtless formed from oxanilide chloride, $\begin{matrix} CCl_2NHC_6H_5 \\ | \\ CCl_2NHC_6H_5 \end{matrix}$, which Wallach did not isolate.

Action of Chlorine on Oxanilide.

In the first attempt to make a chlor-oxanilide, chlorine was passed into a boiling glacial acetic acid solution of oxanilide. There slowly separated what appeared to be small crystalline scales, which the microscope showed to be made of interlaced fibres. The product was filtered, washed with hot glacial acid and alcohol, and dried at 100°. The following is the analysis of the substance, which is designated as preparation *A*.

	Calculated for trichlor-oxanilide.	Found. I.	Found. II.
C_{14}	48.90	48.26	48.58
H_9	2.62	3.03	3.11
Cl_3	31.00	30.88	...
N_2	8.15	8.17	8.26
O_2	9.33	...	...
	100.00		

Too little substance remained for experiments to show

[1] Watts, Dictionary of Chemistry **4**, 286.

[2] Berichte der deutschen chemischen Gesellschaft **12**, 1065; **13**, 527; **14**, 740.

whether it was trichlor-oxanilide or a mixture of equal molecules of dichlor-oxanilide and tetrachlor-oxanilide. As the formation of a compound with two atoms of chlorine in one benzene group, and one atom of chlorine in the other benzene group, of oxanilide is of some theoretical interest, we tried, after having found that prolonged action of chlorine forms a higher chlorinated body, the following experiment: Chlorine was passed into a boiling acetic acid solution of oxanilide until some quantity of scales separated. These were filtered from the hot solution. Chlorine produced in the hot filtrate a precipitate much like the first in appearance, only a little more fibrous. The first product weighed 4.3 grams and yielded 29.02 per cent. of chlorine; the second product weighed 3.5 grams and yielded 34.43 per cent. of chlorine. The determinations correspond to 31.3 per cent. of chlorine in a mixture of the two products, and show the possibility of obtaining a mixture which has the composition of trichlor-oxanilide. Hence the results do prove the formation of this body.

Preparation *B* was made by passing a rapid current of chlorine into a boiling solution of oxanilide in glacial acid. The precipitate, which at first appeared like scales, changed before the stream of chlorine was stopped into a mass of fine white fibres. After the whole mass was cool the product was filtered, washed with alcohol, and dried at 100°. Another preparation, *C*, was made in the same way, only a larger proportion of acetic acid was used, and chlorine was passed into the solution a longer time. The yield of *C* was less than *B*, owing, perhaps, to saponification of the chlor-oxanilide by the long action of the hydrochloric acid in the solution.

	Calculated for tetrachlor-oxanilide.	B.		C.
C_{14}	44.68	46.38	...	46.34
H_8	2.13	2.31	...	2.33
Cl_4	37.23	35.22	35.77	36.36
N_2	7.44	7.75	7.65	7.74
O_2	8.52	...	...	...
	100.00			

The analyses show that the tetrachlor-oxanilide was not free from an oxanilide containing less chlorine. We, however, made from *B* and *C* *m*-dichlor-oxanilic acid, described further on, and *m*-dichlor-aniline, melting at 63°, showing that the tetrachlor-oxanilide made is the meta derivative and has the formula

$$\begin{array}{l} \overset{1}{\text{CO}}\text{NHC}_6\text{H}_3\overset{2}{\text{Cl}}\overset{4}{\text{Cl}} \\ | \\ \underset{1}{\text{CO}}\text{NHC}_6\text{H}_3\underset{2}{\text{Cl}}\underset{4}{\text{Cl}}. \end{array}$$

Tetrachlor-oxanilide dissolves readily in boiling aniline, and is but slightly soluble in boiling absolute alcohol, chloroform, benzene and glacial acetic acid. It dissolves in a hot solution of potassium hydroxide in alcohol, and slowly saponifies. Preparation *C* melted at 255°.

Para-dibrom-oxanilide.

When bromine is added in excess to a boiling glacial acetic acid solution of oxanilide, an abundant precipitation of minute crystals of dibrom-oxanilide soon occurs. The boiling should be continued a few minutes to complete the reaction and to get rid of most of the free bromine. After cooling, the precipitate is filtered and washed with alcohol or water. The acetic acid filtrate contains but little of the anilide. The yield is nearly the theoretical quantity. The substance used for the following analysis was dried at 100°:

	Calculated for dibrom-oxanilide.	Found.	
C_8	42.21	41.71	...
H_{10}	2.51	2.62	...
Br_2	40.20	39.03	38.90
N_2	7.04	7.19	...
O_2	8.04	...	...
	100.00		

The substance yielded, when saponified with a boiling concentrated solution of alcoholic potassium hydroxide, *p*-brom-aniline, melting at 63°, and which gave 8.21 per cent. of nitrogen, theory requiring 8.16 per cent. Bromine, therefore, in acting upon oxanilide in solution, as when acting upon other anilides, takes the para position, thus:

$$\begin{array}{l} \overset{1}{\text{CO}}\text{NHC}_6\text{H}_4\overset{4}{\text{Br}} \\ | \\ \underset{1}{\text{CO}}\text{NHC}_6\text{H}_4\text{Br}. \end{array}$$

Dibrom-oxanilide dissolves in boiling aniline, and is almost insoluble in boiling absolute alcohol and glacial acetic acid, chloroform and benzene. It melts above 300°.

Para-dijod-oxanilide.

10 grams of oxanilide were dissolved in 300 cc. of boiling glacial acetic acid, and 24 grams of iodine were added. No change was apparent. On adding 25 cc. of nitric acid, sp. gr. 1.40, a violent action commenced and continued some minutes, and a crystalline precipitate resulted. It was filtered at once while hot, and washed with alcohol. Its weight after drying was 14 grams, a yield much less than the theoretical. The alcohol used in washing left, on evaporation, a sticky mass. The acetic acid filtrate gave, when diluted with water, a small precipitate, which was not investigated.

The substance used for analysis was dried at 100°:

	Calculated for dijod-oxanilide.	Found.
C_8	34.15	35.98
H_{10}	2.03	2.09
I_2	51.62	50.06
N_2	5.70	6.01
O	6.50	...
	100.00	

Dijod-oxanilide is saponified by a boiling solution of potassium hydroxide in alcohol, with formation of *p*-jodaniline. The substance analysed was salmon-colored, as was another preparation made by passing chlorine into an acetic acid solution of oxanilide containing iodine. It is white after crystallising from a solution in aniline, in which it dissolves abundantly on boiling. Dijod-oxanilide is but slightly soluble in boiling absolute alcohol, chloroform, glacial acetic acid and benzene. It decomposes at high temperatures before fusing.

On the Action of Potassium Hydroxide on Oxanilides.

In attempting to saponify, by means of potassium hydroxide, the tetrachlor-oxanilide of preparation *B*, already described, we obtained a potassium salt which was only slightly soluble in cold water. This led to the study of the action of the alkaline hydroxide upon oxanilide and its halogen derivatives.

The first experiment was as follows: 5 grams of stick potash were dissolved in 200 cc. of boiling alcohol, and 5 grams of oxanilide were added. The latter nearly all dissolved at once. Soon small, lustrous crystals appeared. The boiling was stopped after

five minutes, and the whole was cooled. The crystalline product was filtered and washed with cold alcohol. The filtrate gave a slight precipitate on addition of barium chloride, indicating the presence of no large proportion of oxalic or oxanilic acid. The crystalline product above mentioned was treated with hot water to separate small quantity of unchanged oxanilide. The potassium oxanilate was changed to the less soluble barium salt by adding to the solution barium chloride. A curdy precipitate formed. The whole was heated to boiling to dissolve the barium salt other than oxalate. The clear solution deposited, on cooling, crystals of barium oxanilate, as shown by the following:

	Calculated for barium oxanilate.	Found.
Barium,	29.46	29.27
Nitrogen,	6.02	5.89

Longer boiling, or a more concentrated solution of potassium hydroxide, completely converts oxanilide into aniline. The reaction, therefore, between oxanilide and the alkaline hydroxide takes place in two stages. First, potassium oxanilate and aniline are formed, thus:

$$\begin{matrix}CONHC_6H_5\\ |\\ CONHC_6H_5\end{matrix} + KOH = \begin{matrix}CONHC_6H_5\\ |\\ COOK\end{matrix} + C_6H_5NH_2.$$

The potassium salt is next changed by the potassium hydroxide into potassium oxalate and aniline, as follows:

$$\begin{matrix}CONHC_6H_5\\ |\\ COOK\end{matrix} + KOH \quad \begin{matrix}COOK\\ |\\ COOK\end{matrix} + C_6H_5NH_2.$$

The first reaction is analogous to the formation of ammonium oxamate from ammonia and oxamide. We have also found that the halogen derivatives of oxanilide undergo the same changes and yield oxanilic acids.

Meta-dichlor-oxanilic Acid.

Two preparations of this acid were made from tetrachlor-oxanilide, already described. 4 grams of the anilide were treated in 125 cc. of boiling alcohol with 5 grams of stick potash dissolved in water. The solution, after boiling ten minutes, deposited a small quantity of potassium dichlor-oxanilate. More separated on cooling. It was

filtered, washed with alcohol, and dissolved in small bulk of hot water. From the solution dichlor-oxanilic acid separated as a fibrous mass on addition of hydrochloric acid. It was filtered, washed with water, and dried at 100°. The product was 0.45 gram. In a second trial 3 grams of tetrachlor-oxanilide, 2 grams of potash and 75 cc. of alcohol were taken, and 1 gram of dichlor-oxanilic acid was obtained. The alcoholic filtrate from the potassium dichlor-oxanilate of the first preparation of the acid was evaporated, the residue was washed with water and dried. It melted at 63°, the melting-point of *m*-dichloraniline, and yielded 9.02 per cent. of nitrogen; dichloraniline has 8.65 per cent. The following is the analysis of the dichlor-oxanilic acid:

	Calculated for $CONHC_6H_2Cl_2COOH$.	Found.
C_8	41.06	41.56
H_5	2.14	2.20
Cl_2	30.28	30.10
N	5.99	5.76
O_3	20.53	...
	100.00	

Dichlor-oxanilic acid separates, on cooling a hot, saturated aqueous solution in fibres. 9.71 grams of a solution saturated at 25° left, after evaporation on a water bath, 0.012 gram of residue; hence the acid is soluble in 808 parts of water at 25°. It is soluble in alcohol and ether. It yields, when heated with potassium hydroxide solution, dichloraniline, melting at 63°. Silver nitrate produces in a warm aqueous solution of dichloroxanilic acid a white, flocculent precipitate, which dissolves on boiling, and separates again on cooling. Barium chloride gives a bulky precipitate, soluble in hot water. The silver and barium salts were not further tested. The potassium salt, already alluded to, crystallises, on cooling a hot aqueous solution in white, hair-like fibres. Potassium found, 14.11 per cent.; calculated, 14.29 per cent. Chlorine found, 25.60 per cent.; calculated, 26.05 per cent. Dichlor-oxanilic acid melts at 122°, and at 130° gives off gas slowly.

Para-brom-oxanilic Acid.

When *p*-dibrom-oxanilide is dissolved in a hot dilute solution of potassium hydroxide in alcohol, crystals of potassium brom-oxani-

late soon appear. In one experiment we put 5 grams of dibrom-oxanilide into 200 cc. of boiling alcohol and added a concentrated aqueous solution of 5 grams of stick potash. The anilide dissolved readily, and soon crystals separated. The boiling was kept up five minutes, and then the whole was quickly cooled. The potassium brom-oxanilate was filtered, washed with alcohol, and dissolved in a small quantity of boiling water. The solution, on cooling, deposited the larger portion of the salt. In another experiment 10 grams of dibrom-oxanilide were treated with the quantities of alcohol and potash above mentioned. The boiling was continued five minutes. After cooling, the precipitate was washed with alcohol. The alcoholic filtrate, on boiling again, gave more potassium brom-oxanilate. The first precipitate left, when treated with hot water, much dibromoxanilide, which was added to the filtrate from the second precipitate and converted, by heating, into the potassium salt. The three portions of the salt were united and crystallised from hot water. The yield was 3.26 grams of potassium brom-oxanilate. The mother-liquor, on addition of hydrochloric acid, gave a curdy precipitate of brom-oxanilic acid, which, after washing with cold water and drying at 100°, gave results I. Analysis II was of another preparation of the acid, which was crystallised by cooling a hot aqueous solution.

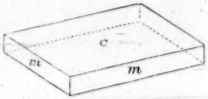
	Calculated for $CONHC_6H_4BrCOOH$.	I.	II.
C_8	39.34	...	39.44
H_4	2.46	...	2.53
Br	32.79	33.09	...
N	5.74	6.08	...
O_2	19.67	...	...
	100.00		

p-Brom-oxanilic acid is soluble in absolute alcohol and ether, and is sparingly soluble in benzene and chloroform. Hot water dissolves it readily, and from the solution, on cooling, crystalline fibres separate. A hot solution was cooled slowly to 25°, and filtered from the crystals which had separated. 9.1047 grams of the solution left, on evaporation on a water bath, 0.0176 gram of brom-oxanilic acid. Hence 1 part of acid is soluble in 515 parts of water at 25°. The solution reacts acid. The acid melts and gives off gases at 198°. It is changed, when heated with potassium hydroxide solution, into *p*-bromaniline.

Brom-oxanilates.

Potassium brom-oxanilate, $CONHC_6H_4BrCOOK$, prepared as already described, gave 13.67 per cent. of potassium, theory requires 13.83 per cent. It crystallises, on cooling a hot aqueous solution in small scales. Mr. S. L. Penfield measured crystals which were obtained from spontaneous evaporation, with the following results.

Crystals are monoclinic, showing simple combinations of prism *m* with base *c*. Habit tabular parallel to *c*. They do not admit of very accurate measurement. The following supplement angles were measured:



$m \wedge m$, $110 \wedge 1\bar{1}0 = 97° 27'$

$c \wedge m$, $001 \wedge 110 = 83°$ (about).

From which the following ratio is calculated:

$$a : b : c = 1.158 : 1 : ?; \quad \beta = 79° 21'.$$

Cleavage very perfect parallel to *c*. Thin tables $\| c$ also cleave very readily parallel to their shorter, less readily parallel to their longer diagonal. Plane of the optic axes the clinopinacoid. In the polarising microscope with convergent light one axis can be seen toward the extremity of the field.

Calcium brom-oxanilate, $(CONHC_6H_4Br)_2Ca$, separates as a white curd on mixing solutions of potassium brom-oxanilate and calcium chloride. It is sparingly soluble in hot water and does not crystallise well. The salt taken for analysis was separated by cooling a hot solution. Calcium found, 7.06 per cent.; calculated, 7.07 per cent.

Silver brom-oxanilate, $CONHC_6H_4BrAg$, forms a white precipitate when silver nitrate is added to solution of brom-oxanilic acid or potassium brom-oxanilate. It is soluble, with partial decomposition, in hot water. Silver found, 30.66; calculated, 30.77 per cent.

Barium brom-oxanilate, $(CONHC_6H_4Br)_2Ba$, forms, when barium chloride is added to solution of potassium, brom-oxanilate. It is sparingly soluble in hot water, and separates in small crystals

when the solution cools. The barium estimations were of two different preparations of crystals which were dried at 100°. The reason for the deficiency in barium was not determined. Barium found, 21.10 and 21.17 per cents.; theory requires 21.99 per cent.

Para-jod-oxanilic Acid.

p-Dijod-oxanilide, 5.24 grams, was added to 100 cc. of boiling alcohol and an aqueous solution of 5 grams of stick potash was added. The dijod-oxanilide dissolved readily, and soon potassium jod-oxanilate separated. The boiling was continued five minutes, and the whole was cooled. The potassium salt was filtered, washed with alcohol, and dissolved in a small quantity of boiling water. The solution, on cooling, deposited potassium jod-oxanilate in small scales. It was filtered, and after drying at 100°, weighed 1.6 grams. Potassium found, 11.89 per cent.; calculated, 11.92 per cent. To the filtrate from the potassium jod-oxanilate hydrochloric acid was added. The bulky white precipitate of jod-oxanilic acid was washed with water and dried at 100°. It weighed 1.4 grams, and gave the following resuts:

	Calculated for $CONHC_6H_4ICOOH$.	Found.
C_8	33.00	33.26
H_6	2.07	2.24
N	4.81	5.18
I	43.62	42.78
O_3	16.50	...
	100.00	

Jod-oxanilic acid melts, with decomposition, at 197–200°. Hot potassium hydroxide solution converts it into *p*-jodaniline. The acid separates in long fibres when a hot solution cools. In one experiment 1 part of jod-oxanilic acid was found to be soluble in 1385 parts of water at 25°. It is soluble in alcohol and ether. Barium chloride and silver nitrate produce precipitates in hot solutions of jod-oxanilic acid.

THE POST-MORTEM DETECTION OF CHLOROFORM.[1]

By Chas. Luedeking, Ph. D.

In an important trial for murder recently held in St. Louis, the author of this paper made a chemical examination of the viscera of the victim, at the request of the coroner, and obtained very decided reactions for chloroform, notwithstanding the fact that the examination was not undertaken until about twelve days after death. The lungs, usually congested in case of death by chloroform, were selected as best suited for its detection. The great volatility of chloroform would seem *a priori* to preclude the possibility of its detection so long after death, and as at the time there was considerable doubt expressed as to the reliability and accuracy of the experiments, the author determined, once for all, to decide the matter by direct experiment, and so set to rest all doubts.

The literature was first scanned carefully to ascertain whether there were any prior experiments in this direction, but nothing could be found. My direct object was then to determine how long after death chloroform can, with certainty, be detected: as also whether or no any substances are generated by the process of decomposition, which might give similar reactions to chloroform, and thus lead to erroneous conclusions.

The manner of experimenting was simple and direct. Dogs of from 15 to 20 pounds weight were destroyed gradually by the administration of chloroform through the lungs in from 5 to 10 minutes. Then the carcasses were allowed to stand in summer's heat or the temperature of the room for different periods of time, and finally the lungs removed and tested for chloroform by the Ragsky method.[2] In the following the experiments are briefly given.

Experiment I.

Carcass exposed on a dissecting table, during full summer's heat, for six days and ten hours. Decomposition far advanced and an exceedingly offensive odor given off. The lungs were removed, and after having been finely minced and rendered *slightly* alkaline by means of sodium carbonate, were heated over a water bath in a flask through which a current of air was slowly passing. The

[1] Presented before the St. Louis Academy of Science, June, 1886.

[2] Erdmann's Jour. **46**, 170.

escaping gases were sent through a Bohemian glass tube, which was heated to bright redness over a space of two inches. The iodised starch paper was five inches distant from this heated portion of the tube, and throughout the experiment remained perfectly cool.

A very strong bluing of the paper was observed and the nitrate of silver solution was strongly precipitated.

Experiment II.

Carcass exposed during full summer's heat for ten days. It had then lost all solidity, the hair literally falling off by the slightest abrasion. The lungs were removed and examined as in Experiment I. A very decided reaction for chloroform was obtained.

Experiment III.

Carcass exposed during full summer's heat for fourteen days. The lungs then removed and examined as in Experiment I. The reaction for chloroform was very decided.

Experiment IV.

Carcass placed in an ice-chest for three weeks, and then exposed for ten days during full summer's heat. The lungs were then examined as in Experiment I, and a strong reaction for chloroform obtained.

I do not hesitate to say that in winter chloroform could be detected without the slightest difficulty for many months after death.

Experiment V.

Carcass exposed in a room (70° F., very constant) for three weeks and three days. The lungs were then examined as in Experiment I, and a very decided reaction for chloroform obtained.

Experiment VI.

Carcass exposed in a room (70° F., very constant) for four weeks. The lungs examined as in Experiment I, and a decided reaction for chloroform obtained.

The question now arises whether there cannot be substances formed by the process of decomposition, which, resembling chloroform in certain chemical reactions, might therefore lead to erroneous

conclusions. Dr. Ragsky already partially answered this question experimentally. The author made three experiments to this end, which are herewith briefly given.

Experiment I.

The lungs of a slaughtered bull exposed during full summer's heat for ten days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

Experiment II.

The lungs of a slaughtered bull exposed during full summer's heat for fourteen days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

Experiment III.

Carcass of a dog destroyed by coal gas was exposed in a room (70° F., very constant) for three weeks and four days. No chloroform reaction could be obtained by the Ragsky method.

Conclusions.

1. By the process of decomposition no substances are generated which could vitiate the tests for chloroform by the Ragsky method.

2. Chloroform, when it has caused death by inhalation, can with certainty be detected in the body four weeks after death, and, notwithstanding its volatility, it is certainly retained in the viscera in large amount during this time.

In the case which was the cause of these experiments being undertaken, the victim had been dead at least ten days before the body was discovered, in high state of decomposition. On the strength of the Ragsky and Hofmann tests the author gave it as his sworn opinion that the deceased had chloroform in his viscera, whereupon a charge of murder by chloroform was preferred. Maxwell, the culprit, finally, after the lapse of an entire year, made confession that chloroform had indeed been the cause of death.

It being certain, finally, that chloroform can be detected a long time after death, as evidenced by our experiments, we must next try to understand why this should be so. The following may serve to this end.

R. Dubois[1] finds that the vapor of chloroform penetrates into the interior of the tissues, and becomes substituted for normal water. This is not a phenomenon of desiccation or osmose; a true affinity comes into play, the protoplasm absorbing the vapor of the anaesthetic and expelling a certain quantity of water.

Chancel and Parmentier[2] have proven that chloroform has a very decided affinity for water.

The author allowed to stand open a flask containing water, holding a small quantity of chloroform in solution. After two weeks' time the chloroform reactions could still be obtained without any difficulty.

Add to the above that chloroform is a powerful preservative agent,[3] we have a collection of factors sufficient to enable us to understand the lengthy occlusion of chloroform in the animal body, though others of minor importance might be adduced besides these.

Grehaut and Quinquand,[4] experimenting on dogs, find the amount of chloroform necessary to produce anaesthesia to be at least one gram to every two litres of blood. On the basis of these results, the total quantity of chloroform in the blood of a man of 150 pounds weight would be 2¾ grams approximately, when rendered insensible through its inhalation. The amount necessary to produce death would, under normal conditions, certainly not be less than this. Under the assumption that one-sixth of the entire quantity of blood circulating in the body is at all times passing through the lungs, the quantity of chloroform in the lungs of a man of 150 pounds weight, rendered insensible from its inhalation, would be about one-half gram.

We desire to emphasise by this calculation that there is an abundance of material in the lungs for the detection of chloroform. The liver would undoubtedly also be very suitable for its detection.

LABORATORY WASHINGTON UNIVERSITY, ST. LOUIS, MO.

[1] Chem. News, 1886, 311. [2] C. R. **100**, 27.
[3] Robin and Augendre, C. R. **30**, 52; **31**, 679. [4] C. R. **97**, 753.

ON THE ACTION OF HEAT UPON ETHYLENE.

By L. M. Norton and A. A. Noyes.

In a number of cases where an organic compound consisting largely of carbon and hydrogen has been decomposed by the action of heat, a certain hydrocarbon called crotonylene, C_4H_6, has been observed among the products. It accompanies ethylene frequently when this gas is formed by the action of heat, and its formation has not been observed in any case where ethylene was absent. Thus it is found in illuminating gas,[1] and although it is present in small quantities, yet upon its presence and that of benzol depends to a great degree the illuminating power of coal gas. It seemed of interest to inquire whether this important hydrocarbon was a primary product of decomposition by heat, or a secondary product formed by the action of heat upon ethylene. As the formation of crotonylene by the action of heat upon ethylene alone had never been observed, we have once more passed a current of ethylene through a red-hot tube and examined the products. This subject was first carefully investigated by Marchand,[2] who obtained from ethylene, at a white heat, carbon and hydrogen; then by Magnus,[3] who obtained, at a red heat, methane, hydrogen, carbon and naphthalene. Berthelot,[4] in several investigations, obtained acetylene, ethane, benzol, styrolene and naphthalene.

The ethylene used in our investigation was prepared by the action of sulphuric acid upon alcohol,[5] was purified and stored in large gas-holders. After drying, it was passed slowly through a piece of hard glass tube 15 mm. in diameter, which was maintained at a low red heat for a distance of 60 cm. The products issuing from this tube passed first through a series of U tubes which were surrounded by a freezing mixture. The uncondensed products passed then through an ammoniacal cuprous chloride solution to absorb hydrocarbons of the acetylene series, and then through bromine to absorb hydrocarbons of the ethylene series, and samples of the unabsorbed gases were finally collected over water at the end of the apparatus.

[1] Berthelot, Comptes Rendus **82**, 930; Tieftrunk, Jour. f. Gasbeleuchtung, 1877, 509; Helbing, Ann. d. Chem. **172**, 281.

[2] J. prak. Chem. **26**, 478. [3] Pogg. Ann. **90**, 1. [4] Comptes Rendus **50**, 805; **62**, 94. Ann. d. Chim. et Phys. **4**, 16, 144, etc.

[5] Erlenmeyer and Bunte, Ann. d. Chem. **168**, 65.

Carbon was deposited in the decomposition tube. A liquid slowly condensed in the U tubes. At the end of one month 15 cc. had been collected. This liquid was divided into four portions, boiling 75°–130°, 130°–230°, 230°–330°, 330°–430°. The portion boiling 75°–130° gave a large fraction boiling from 80°–100°, which solidified in a freezing mixture and was proved, by its specific gravity and the aniline test, to be benzol. A white crystalline solid was obtained from the portion boiling from 130° to 230° which melted at 79° after sublimation, and was naphthalene. A crystalline substance separated from the portion boiling 230° to 330° which, after sublimation, melted at about 200°, and was probably anthracene. Other aromatic hydrocarbons were present in the liquid, but in quantities too small for identification. Faint traces only of a precipitate were found in the ammoniacal cuprous chloride solution. If hydrocarbons of the acetylene series were formed, they must have been immediately destroyed in the hot tube. About 300 grams of bromides of unsaturated hydrocarbons were obtained. These bromides consisted of a mixture of liquid bromides and a solid bromide. Upon distillation the latter remained in the flask. The liquid bromides consisted largely of ethylene bromide from the absorption of undecomposed ethylene. Fractionation and analysis showed that they also contained methylene bromide from the action of bromine on methane,[1] propylene bromide and butylene bromide from the absorption of propylene and butylene by the bromine.

The solid bromide was purified by crystallisation from alcohol and by sublimation, and the analysis then gave the following result:

	Found.	Calculated for tetrabrombutane or crotonylene tetrabromide.
Br	85.66	85.56

This bromide agrees in all its properties with the crotonylene tetrabromide prepared in this laboratory by passing illuminating gas through bromine, and which melts at 115½°, and is also identical with that obtained from the products formed by the action of heat upon hexane and pentane,[2] and without doubt with that obtained by Henninger[3] from the crotonylene from erythrite, and by Armstrong and Miller[4] from the crotonylene from oil gas, and which possesses the constitution $CH_2Br—CHBr—CHBr—CH_2Br$. The

[1] Moore, Report on Granger Water Gas, Phil., 1885, 26.
[2] Norton and Andrews, this Journal **8**, 1. [3] Bull. Soc. Chem. [2] **19**, 145.
[4] Jour. Chem. Soc., 1886, 74.

crotonylene formed by the action of heat upon ethylene is therefore divinyl, $CH_2=CH-CH=CH_2$, and it appears probable that its frequent occurrence is to be explained by the equation $2C_2H_4 = C_4H_6 + H_2$. An analysis by explosion of the gases collected over water at the end of our apparatus showed that they consisted of methane and ethane.[1] The products obtained by us by passing ethylene through a red-hot tube and identified were therefore benzol, naphthalene, anthracene (?), propylene, butylene, divinyl, methane, ethane and carbon. Berthelot[2] is of the opinion that the formation of aromatic derivatives from ethylene under the influence of heat is primarily due to the aggregation of molecules of acetylene, and that acetylene is first formed from the ethylene. Jacobsen[3] believes that all aromatic compounds formed by dry distillation originate in compounds of the acetylene series, but he offers no new evidence to sustain his views. The absence of acetylene from the products which we obtained by the action of heat on ethylene shows that, if these views are correct, the circumstances of our experiment must have favored the formation of aromatic derivatives to an extraordinary degree. We incline rather to the view that benzol is formed directly by the action of heat upon ethylene. Furthermore, Armstrong[4] states that Messrs. Thorp and Dyson have again subjected acetylene to the action of heat, and that they find it exceedingly difficult to obtain even a very small quantity of benzol in this way. We propose to extend our investigation to the higher homologues of ethylene.

Massachusetts Institute of Technology, Boston, *June*, 1886.

Contributions from the Chemical Laboratory, U. S. Department of Agriculture.

VIII.—VARIATIONS IN THE CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF AMERICAN OATS.

By Clifford Richardson.

In a previous paper[5] a study of the effect of environment on wheat and corn was presented, showing the effect, to a greater or less degree, upon the grain of these two cereals which season,

[1] Day, this Journal **8**, 165. [2] *Loc. cit.* [3] Berichte d. deut. chem. Gesell. **10**, 853.
[4] Jour. Soc. Chem. Ind., 1884, 466. [5] This Journal **6**, 302–317.

climate, soil and other conditions exert. Since that time our investigations have been extended to oats, with results which have recently appeared in detail in Bulletin No. 9 of the Division of Chemistry of the Department of Agriculture of the United States. Of the cereals first examined wheat was found to be far more susceptible to its environment than corn, and in the present investigation it appears that oats are in their nature somewhat different from either of these grains in their mode of response to controlling causes.

This grain is grown under as varied conditions as any cereal, and in appearance is most variable. They will grow and can be made to pay on almost any soil and in all parts of the country, with the result that in weight per bushel and size of the grain and other physical properties there are found the greatest differences. It was reasonable to suppose that the composition of the grain would vary in the same way. This has, however, proved to be dependent on its environment less than wheat.

One hundred and sixty-six specimens of oats have been collected from all parts of the country, and from their examination the following facts have been learned.

In the North white or yellow, black and white, and black oats are principally grown. In the South varieties of the red rust proof are the prevailing crop. In the North the seed is put in in April or May, and harvested in July or August. In the South it is sown in November to January, and harvested in May or June, the growth being made in the cool part of the year. In certain intermediate localities, where the summers are too dry and hot and the winters too cold, it is difficult to do anything with this grain.

The difference in appearance between the crops of these two sections of the country is marked. The Southern oats are large, light, awned varieties, of reddish-brown color, with inflated husks not nearly filled by the kernel. The Northern grain is smaller, more compact, not often awned, and with the husk in the better samples well filled out.

Notwithstanding these characteristics, we learn from averages of the results that the size and weight of the Southern clean kernel are rather larger than the Northern. Their fluffy husk, however, makes them lighter oats in weight per bushel.

Averages have been calculated for various sections as follows: The Northern States include all north of Maryland and Kentucky, together with Missouri, Montana and Dakota; the Southern, all south of these; and the Pacific slope, Colorado, Nevada, New

Mexico, Washington Territory, Oregon and Utah; the Atlantic slope consists of the States east of the Ohio river and the Gulf; the Western States, of those west of this line, excepting those on the Pacific slope.

Average Physical Properties of Oats.

State.	Number of specimens.	Weight of 100 kernels.	Clean grain.	Hulled grain.	Hulls.	Weight per bushel.
			Per cent.	Per cent.	Per cent.	Lbs.
United States	166	2.507	95.00	69.97	30.03	37.2
Northern States	90	2.290	95.63	70.60	29.30	38.0
Southern States	66	2.028	94.18	69.08	30.92	34.5
Pacific Slope	20	2.737	94.93	69.52	30.48	43.2
Atlantic Slope	58	2.523	95.37	69.69	30.31	37.0
Western States	61	2.339	95.82	72.20	27.80	37.8
Maine	3	2.344	97.38	70.29	29.71	38.6
New Hampshire	3	2.472	93.83	71.54	28.46	38.3
Vermont	4	2.474	94.97	69.52	30.48	39.4
Connecticut	4	2.110	95.78	67.44	32.56	35.6
Rhode Island	1	3.029	97.16	67.27	32.73	32.3
New York	8	2.571	95.32	71.00	29.00	39.8
New Jersey	2	2.371	98.50	72.75	27.25	36.6
Pennsylvania	4	2.686	92.24	68.55	31.45	38.0
Ohio	9	2.256	96.42	71.44	28.56	39.8
Michigan	6	2.767	96.22	72.31	27.69	42.3
Indiana	3	2.188	93.36	72.00	28.00	36.7
Illinois	9	2.350	97.21	72.02	27.98	39.4
Wisconsin	5	2.487	94.81	70.77	29.23	39.0
Minnesota	9	2.416	96.09	71.67	28.33	43.6
Iowa	6	2.245	96.99	71.63	28.37	38.4
Missouri	3	1.867	98.13	69.78	30.22	37.8
Nebraska	3	1.763	97.87	70.10	29.90	33.1
Dakota	5	2.519	92.92	66.20	33.80	43.3
Montana	3	2.410	91.06	70.54	29.46	30.0
Maryland	2	2.244	93.26	71.53	28.47	37.5
Delaware	1	1.976	98.04	69.69	30.41	.....
Virginia	3	2.657	94.67	65.23	34.77	39.2
West Virginia	4	2.500	95.94	66.48	33.52	39.2
North Carolina	6	2.496	94.52	70.37	29.63	39.8
South Carolina	8	2.767	95.99	69.52	30.48	38.4
Kentucky	4	2.249	94.88	69.99	30.01	31.7
Tennessee	4	2.089	95.66	65.42	34.58	36.3
Georgia	7	2.609	93.39	68.56	31.44	31.6
Florida	5	2.542	97.79	68.94	31.06	29.0
Alabama	5	2.961	96.47	68.17	31.83	31.7
Mississippi	5	2.751	90.40	70.52	29.48	34.4
Louisiana	3	2.957	94.99	69.90	30.10	36.9
Arkansas	1	2.760	97.08	64.10	35.90	35.2
Colorado	3	2.442	90.16	69.80	30.21	43.3
Texas	8	2.924	96.29	71.56	28.44	36.1
Utah	1	2.560	90.72	61.17	38.83	43.5
Nevada	1	2.019	95.05	66.01	33.99	41.8
New Mexico	1	2.462	97.67	73.21	26.79	41.4
Washington Territory	2	3.602	98.34	76.10	23.90	43.1
Oregon	2	3.279	96.97	66.12	33.88	45.6

Oats having the husk (pallets and at times glumes) are necessarily lighter than wheat in weight per hundred grains. The heaviest is from the Pacific slope, and the South ranks next, owing, as has been said, to its large size. In weight per bushel, however, the fluffy husk of the Southern grain makes it the lowest in the country, while the Pacific slope retains the highest weight per bushel, as also size and weight per 100, showing it to have a plump, well-filled grain.

The average for the country, 37.2 pounds, appears rather high in comparison with the most common legal weight, 32 pounds, but the determinations have been proved correct for the specimens examined, and are not mere estimates. The samples are, too, apparently fair averages, as the figures giving percentages of clean grain in the specimens as received show that no particular pains were taken to prepare them for exhibition before reaching us. The range with this cereal is larger than with any other. The extremes in weight per 100 grains were, for the lightest, from Nebraska, 1.582 grams, and from Oregon, for the heaviest, 3.786 grams. Cleanliness varied from 99.8 per cent. to 70.0 per cent., but of course had nothing to do with locality. The heaviest weight per bushel was found in specimens from Colorado and Dakota, weighing 48.8 and 48.6 pounds. The lightest were from Alabama and from Florida, 24.7 and 26.9 pounds respectively.

In milling oats the relation of kernel to waste is about one-half. Our results show that the relation of kernel to husk averages for the whole country 7 to 3, those from the Western States being a little less husky, and those from the South considerably more so. It is, however, the inflated nature of the husk in the Southern grain and the fact that the glume or outer husk is often adherent that affects the weight per bushel more than the slightly larger proportion.

The extremes found were 79.28 per cent. of kernel in a specimen from Washington Territory, and 55.37 per cent. in one from Dakota. Washington and Oregon sustain their reputation for fine looking grain, while the small proportion of kernel in the Dakota specimen is due entirely to harvesting before it was quite ripened. It is hardly a fair example, other specimens from the Territory reaching over 70.0 per cent. of kernel.

In weight per bushel the warm climate of the South so affects the form of the grain as to lower its average 2.7 pounds. This is

hardly as large as would be expected, and leads to the conclusion that the climate has a greater effect than some other characteristics. One of these is yield, which, from an average of 30 bushels in the North, falls to about 10 in the South, and, as has been said, the color and shape of the grain are much changed.

The variations in composition which correspond to those in physical properties have been derived in a similar way by analyses of the same samples separated into kernels and hulls. This separation was primarily undertaken to determine the relation of the two portions of the grain, and the analyses were completed of each part, in order that comparison with wheat and of the kernels among themselves might not be influenced by the presence of the husks.

The averages derived from the analyses are as follows:

Average Composition of American Oats, arranged by States.

State.	Number of analyses.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.
United States	179	6.93	2.15	8.14	67.09	1.38	14.31	2.28
Atlantic Slope	64	6.84	2.17	8.22	67.10	1.37	14.30	2.28
Northern States	92	7.07	2.19	8.02	66.88	1.37	14.47	2.32
Western States	54	6.98	2.19	7.91	67.06	1.37	14.49	2.32
Southern States	69	6.79	2.12	8.23	67.22	1.35	14.29	2.28
Northwestern States	8	7.38	2.23	8.54	66.96	1.28	13.61	2.18
Pacific Slope	18	6.71	2.10	8.87	67.78	1.53	13.01	2.08
Maine	3	7.19	1.91	8.55	66.40	1.77	14 18	2.27
New Hampshire	3	7.06	2.30	8.36	65.27	1.32	15.69	2.51
Vermont	4	6.33	2.00	8.06	66.15	1.34	15.62	2.50
Connecticut	4	6.54	2.30	8.06	68.07	1.47	13.56	2.17
Rhode Island	1	7.52	2.02	8.71	68.66	1.01	12.08	1.93
New York	9	7.46	2.14	8.02	66.53	1.44	14.41	2.31
New Jersey	2	7.42	2.29	7.14	66.55	1.29	15.31	2.45
Pennsylvania	4	7.10	2.36	8.00	65.85	1.32	15.37	2.46
Ohio	9	6.76	2.25	8.32	65.39	1.19	16.09	2.57
Michigan	6	7.11	2.35	7.74	67.61	1.19	14.00	2.24
Indiana	3	8.05	1.92	7.82	65.69	1.24	15.28	2.45
Illinois	9	6.19	2.34	7.64	67.69	1.55	14.59	2.34
Wisconsin	5	7.27	2.06	7.45	68.46	1.49	13.27	2.12
Minnesota	9	7.16	2.27	7.91	68.33	1.30	13.03	2.09
Iowa	7	7.01	2.03	8.02	66.72	1.44	14.78	2.37
Missouri	3	7.11	1.91	8.35	65.54	1.51	15.58	2.49
Nebraska	3	7.42	2.16	7.98	66.64	1.51	14.29	2.29
Dakota	5	6.74	2.25	8.16	67.39	1.28	14.28	2.27
Montana	3	8.44	2.20	9.18	66.23	1.29	12.66	2.03
Maryland	2	7.01	2.36	7.91	66.39	1.46	14.87	2.38
Delaware	1	5.94	2.27	7.75	66.09	1.35	16.60	2.66
Virginia	4	6.63	2.43	7.93	66.03	1.49	15.49	2.48
West Virginia	4	6.64	2.29	7.51	64.86	1.46	17.24	2.76
North Carolina	6	6.84	2.06	8.27	68.28	1.63	12.92	2.07
South Carolina	8	7.07	2.09	8.48	68.19	1.00	13.17	2.11
Kentucky	4	7.34	2.10	7.80	65.97	1.74	15.05	2.41
Tennessee	4	6.81	2.22	8.09	67.33	1.42	14.13	2.26
Georgia	8	6.15	2.28	8.54	67.65	1.35	14.13	2.26
Florida	5	6.03	2.08	8.49	67.85	1.37	14.18	2.27
Alabama	5	6.40	1.94	8.42	67.55	1.16	14.53	2.33
Mississippi	5	7.41	1.97	7.86	67.48	1.28	14.00	2.24
Louisiana	3	8.12	2.13	8.09	66.55	1.17	13.94	2.23
Arkansas	2	5.80	1.12	7.92	67.59	1.78	14.79	2.37
Texas	8	7.16	2.04	8.71	67.08	1.21	13.80	2.21
Colorado	4	6.06	2.31	7.80	67.50	1.10	15.23	2.44
Utah	2	6.67	2.39	8.49	68.30	1.72	12.43	1.99
Nevada	1	6.80	2 27	9.72	66.21	1.17	13.83	2.21
New Mexico	2	6.83	2.31	9.66	66.16	1.73	13.31	2.14
Washington Territory	2	6.82	1.67	9.28	69.96	1.51	10.76	1.72
Oregon	2	6.86	2.35	8.38	67.77	1.78	12.86	2.06
California	5	7.08	1.76	9.40	67.90	1.71	12.15	1.94

Average Composition of Hulls of Oats, arranged by States.

State.	Number of analyses.	Water.	Ash.	Undetermined.	Fibre.	Albuminoids.	Nitrogen.
United States	100	5.22	5.59	68.83	17.88	2.48	.40
Atlantic Slope	43	4.73	4.78	70.35	17.50	2.64	.42
Northern States	52	4.89	5.69	68.52	18.42	2.48	.40
Western States	33	4.99	6.39	67.88	18.30	2.44	.39
Southern States	43	5.71	5.40	69.20	17.15	2.54	.41
Northwestern States	17	4.57	6.25	68.80	18.35	2.03	.33
Pacific Slope	2	5.16	5.98	67.87	19.15	1.84	.30
Maine	1	4.00	4.30	65.99	23.36	1.75	.28
New Hampshire	3	4.88	4.62	68.19	19.62	2.69	.43
Vermont	4	4.15	4.19	71.08	18.08	2.50	.40
Connecticut	3	5.98	4.70	67.40	19.35	2.57	.41
Rhode Island	1	5.00	4.50	73.12	15.10	2.28	.36
New York	3	4.73	4.43	71.54	16.44	2.86	.40
New Jersey	1	2.90	6.30	68.46	19.19	3.15	.50
Pennsylvania	3	4.28	4.00	69.92	19.47	2.33	.37
Ohio	6	4.51	6.00	69.05	17.84	2.60	.42
Michigan	4	4.51	5.44	68.36	19.67	2.02	.32
Indiana	1	4.80	5.20	68.17	19.38	2.45	.39
Illinois	6	7.01	6.85	64.90	18.43	2.81	.45
Wisconsin	4	3.71	6.58	70.22	17.48	2.01	.32
Minnesota	4	5.24	6.43	67.28	18.77	2.28	.36
Iowa	2	5.25	6.43	67.04	19.18	2.10	.34
Nebraska	1	4.10	7.80	68.40	17.60	2.10	.34
Missouri	2	4.72	6.23	69.85	16.22	2.98	.48
Dakota	1	5.40	7.70	66.50	18.12	2.28	.36
Montana	2	7.40	6.99	68.04	18.38	2.89	.46
Maryland	2	4.20	5.12	66.24	20.94	3.50	.56
Virginia	3	4.08	4.37	69.77	19.03	2.75	.44
West Virginia	2	4.03	4.60	69.85	19.16	2.36	.38
North Carolina	5	5.02	5.92	70.48	15.78	2.80	.45
South Carolina	5	4.23	5.64	73.47	13.93	2.73	.44
Kentucky	3	10.80	5.00	60.87	20.18	3.15	.50
Tennessee	2	6.88	6.00	66.61	18.24	2.27	.36
Georgia	6	5.53	5.13	69.51	17.28	2.57	.41
Florida	3	4.86	2.19	74.44	15.51	2.28	.36
Alabama	2	9.72	4.98	65.68	17.43	2.19	.35
Mississippi	2	5.30	7.28	67.95	17.19	2.28	.36
Louisiana	2	10.30	4.90	63.38	19.23	2.19	.35
Arkansas	1	6.00	5.14	69.08	16.80	2.98	.48
Texas	5	4.06	7.22	71.01	15.96	1.75	.28
Colorado	2	4.17	6.62	66.82	20.03	2.36	.38
Washington Territory	1	5.20	7.16	67.37	18.34	1.93	.31
Oregon	1	5.12	4.80	68.37	19.96	1.75	.28
California	1	4.20	6.02	71.63	16.40	1.75	.28

The chemical composition of the specimens appears from the preceding data to be rather surprising. It was reasonable to suppose that as oats deteriorate so readily, and are apparently so easily influenced by their environment, as great variations would be found in their composition under different climatic conditions as is the case with wheats, and as would correspond to the great differences in the physical character of the samples. From the one hundred and sixty-six analyses which have been made, we learn that there is not that variation in the oat kernel itself which was expected to be due to climatic condition. The proportion of husk to kernel and the compactness of the grain prove to be the all-important factors, and the weight per bushel the best means of judging of the value of the grain.

The only peculiarities noticed are that the eighteen specimens from the Pacific slope are lower in albuminoids and richer in fibre than the averages for other parts of the country. The average for the hulls from the West shows the presence of more ash than in those from the East, and more fibre, and, like the kernels, they are slightly deficient in albuminoids. Actual analysis of the mixed remainder from the individual analyses of the hulls furnished the following results:

	North. Per cent.	South. Per cent.	West. Per cent.
Water,	7.71	7.83	8.10
Ash,	5.57	5.50	6.22
Oil,	.79	.74	1.01
Undetermined,	62.47	63.84	60.09
Crude fibre,	20.83	19.64	21.45
Albuminoids,	2.63	2.45	3.13
	100.00	100.00	100.00

The small number from the West contained rather more albuminoids than the average results for that part of the country, but for the other sections there is a close agreement. In these samples, oil was determined and found to be extremely small in amount, following the percentage of albuminoids, the largest amount of both of these constituents being in the Western hulls, and there seems to be a more or less intimate connection between them.

Of all the cereals this is the richest in oil and albuminoids, the average for the former being 8.14 per cent. and for the latter 14.31; of course diminished relatively in the grain as fed, the average

composition of which would probably be, as calculated from the average for each portion—

	Kernel. Per cent.	Hull. Per cent.	Whole grain. Per cent.
Water,	4.85	1.57	6.42
Ash,	1.50	1.68	3.18
Oil,	5.70	.24	5.94
Carbhydrates,	46.96	20.41	67.37
Crude fibre,	.97	5.36	6.33
Albuminoids,	10.02	.74	10.76
	70.00	30.00	100.00

An average of 20 analyses of oats in the husk given by Brewer and 153 given by Koenig is given as follows for comparison:

	Brewer. Per cent.	Koenig. Per cent.	Richardson. Per cent.
Water,	10.56	12.37	6.42
Ash,	2.95	3.02	3.18
Oil,	4.97	5.23	6.64
Carbhydrates,	61.10	57.78	66.67
Crude fibre,	9.01	11.19	6.33
Albuminoids,	11.41	10.41	10.76

The average albuminoids in the grains as fed, calculated in this same manner, are as follows for different sections:

Northern States, . . .	10.96 per cent.
Southern States, . . .	10.66
Pacific Slope, ...	9.60
Atlantic Slope, ...	10.76
Western States, . . .	11.24

The lowness of the Pacific slope is purely climatic, as has been found to be the case with all the cereals. In appearance the oats from that section are the finest. The fullness of the husk in the Western States or the plumpness of the grain makes this the richest in albuminoids as it is fed. The South is poorest, for reasons which have been mentioned. That these figures are entirely dependent on the percentage of husk, and not on peculiarities of the kernel, a study of their analyses will show; for, among 179, only 3 fell below 10 per cent. of albuminoids, 4 below 11 per cent., and 12 below 12 per cent., while at the same time only 13 are above 17 per cent., and 23 above 16 per cent.; that is

to say, all but 28, or 84.4 per cent., are within the limits of 12 and 16 per cent., a small variation, although the albuminoids are higher in amount than wheat; and as the averages for the different States and sections of the country do not vary far from 14.3 per cent., with the exception of the Pacific coast, oats cannot be said, as far as the grain itself is concerned, to be in chemical composition very susceptible to their environment, although extremes widely apart are found.

These were as follows:

Extremes in Composition of Kernels of Oats.

	Highest.	State.	Lowest.	State.
	Per cent.		Per cent	
Water	11.13	Montana	4.67	Arkansas.
Ash	2.94	Michigan	.87	Iowa.
Oil	11.20	Texas	6.50	Virginia.
Carbhydrates	71.91	North Carolina	62.82	Texas and Missouri.
Crude fibre	2.08	Kentucky and Oregon	.88	South Carolina.
Albuminoids.	19.44	Ohio	9.10	North Carolina.

The highest percentage of albuminoids was 1.41 per cent. higher than has been found in any other cereal in this country, and the lowest 2 per cent. higher than the lowest percentage in wheat.

The analyses of the heaviest and largest, of those having the greatest and least weight per bushel, of those having highest and lowest percentage of albuminoids, and of the smallest in size and in weight per bushel, have been selected as a study of the effect of these contrasts on the chemical composition.

Composition of Specimens Exhibiting Extreme Characteristics.

	Serial number.	State.	Weight of 100 kernels.	Husk.	Weight per bushel.	Water.	Ash.	Oil.	Carbhydrates.	Crude fibre.	Albuminoids.
			grams	per ct.	lbs.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Smallest	3200	Nebr	1.512	31.21	29.7	7.32	2.24	8.72	66.39	1.33	14.00
Largest	3277	Oreg	3.786	40.85	43.3	7.01	2.42	7.87	66.80	2.07	13.83
Cleanest	3041	Fla	2.880	32.87	31.5	5.83	2.52	7.68	68.93	1.56	13.48
Chaffiest	3185	Miss	2 113	25.40	38.2	7.05	2.10	7.81	67.32	1.54	14.18
Highest per cent. of kernel	3435	Wash	3.148	20.72	43.2	6.55	1.55	10.57	68.36	1.07	11.90
Lowest per cent. of kernel	3391	Dak	2.372	44.63	38.8	8.75	2.15	9.47	66.17	1.56	11.90
Highest albuminoids	3262	Oh o	2.630	39.17	40.0	6.78	2.07	7.40	63.21	1.10	19.44
Lowest albuminoids	3249	N. C	2.060	29.50	47.8	7.78	2.02	7.32	71.91	1.87	9.10
Heaviest weight per bushel	3020	Col	2.958	30.24	48.8	4.80	2.08	7.27	66.82	1.00	18.03
Lightest weight per bushel	3002	Ala	3.068	31.66	24.7	6.59	1.80	8.98	66.20	1.20	15.23
Average weight for U. S.		U. S	2.507	30.03	37.2	6.93	2.15	8.14	67.09	1.38	14.31

From the preceding figures nothing can be deduced which shows any such difference as we might expect between the largest and smallest oats, between the cleanest and most chaffy, or between those having the highest and lowest proportion of kernel in the grain. The weight per bushel of the specimen having the lowest percentage of albuminoids is extraordinarily high, while that containing the highest percentage is also above the average. Differences, too, between the weights per bushel of the extreme specimens are in nowise connected with their chemical composition. The largest and one of the finest and heaviest oats from Oregon had nearly the maximum of husk, and, while the lowest proportion of husk corresponded, of course, with a high weight per bushel, the largest proportion of husks was coincident with a weight per bushel above the average.

An immense number of conditions seem, therefore, to affect the characteristics of this grain, and while in many ways, at first glance, from its chemical composition, it seems to be less changeable than one would expect, on examination it seems to be quite largely influenced by all the circumstances of its environment, and more especially in its physical character.

The investigation has extended only to the crop of one year, and it would be necessary, for a thorough knowledge of the habits of this cereal, to follow it in a number of localities for a series of years, as has been done with wheat.

Maercke, in Germany, has followed out this subject under the conditions there existing, and has published some extremely interesting results in the *Zeitschrift des landwirthschaftlichen Verein der Provinz Sachsen*, which are worthy of careful study.

WASHINGTON, D. C., *May*, 1886.